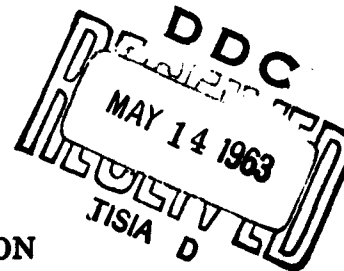63-3-4

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RESEARCH ON HYDROGEN OVERVOLTAGE ON METALLIC SINGLE CRYSTALS

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Milano (Italy)

FEBRUARY 1961

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WRIGHT AIR DEVELOPMENT DIVISION

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WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by Laboratori di Elettrochimica, Chimica Fisica e Metallurgia del Politecnico di Milano - Milano, Italy under USAF Contract No. AF 61(052)-144. The contract was initiated under Project No. 7022, "Surface & Interface Phenomena of Matter", Task No. 73660, "Cathodic Processes Which Involve Release of Hydrogen". It was administered under the direction of Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Dr. J. R. Barton acting as project engineer.

The work on this report was conducted from July 1959 to July 1960.

WADD TR 60-769

ABSTRACT

Hydrogen overvoltage on silver, lead, nickel, tin and cadmium single crystals has been measured in different experimental conditions. The results have been discussed and it has been observed that the Tafel law is generally followed.

PUBLICATION REVIEW

This report has been reviewed and is approved.
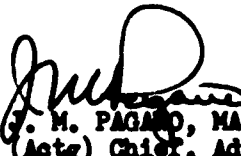
FOR THE COMMANDER:

J. M. PAGANO, MAJOR USAF
(Actg) Chief, Advanced Metallurgical
Studies Branch
Metals and Ceramics Laboratory
Materials Central

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I. Introduction

Research work on the hydrogen overvoltage has been frequently reported in the literature, particularly for the most common metals as those examined by us.

It maybe of interest to consider at first the research, which compared the behavior of many different metals in the same solution under the same experimental conditions.

Hickling and Salt (1) carried out hydrogen overvoltage measurements in the c.d. range from 10 to 10^3 A/m^2 in M HCl solution, for a wide variety of cathode materials among them the ones we are interested for: silver, lead and tin in the form of rods and Ni and Cd as thin films produced by electrodeposition.

Ni, Fe, Bi, W, Au and Pt gave straight line overvoltage - log c.d. graphs, as required by Tafel's equation.

Ag, Pb, Sn, Cd and others showed deviations from this equation, there being a general tendency for the overvoltage to approach a constant value in each case at high c.d.

Frumkin (2) criticized these results and maintained that the reported deviations from the logarithmic relation were due to the commutator method of determination.

With this method, polarizing current was continuously interrupted during hydrogen overvoltage measurements.

Indeed, Pecherskaya and Stender (3) using the direct method and working under the same conditions, found that also in the higher c.d. range, the Tafel law is followed by the above metals with low slope values.

The results are valid also for 1 M H_2SO_4 solutions (4).

For alkaline solution (0, 6 and 6 N NaOH) Zholuder and Stender (5) found that the Tafel law is followed in the same c.d. range with greater b values than in acid solutions and that the overvoltage values increase in the following order: Ni, Ag, Cd, Sn and Pb; whereas in sulfuric acid solution

the order is the same for c. d. up to 10^2 A/m^2, but owing to the higher cadmium slope, overvoltage on cadmium electrodes become greater than on tin electrodes above this value.

Let us now examine in some detail the results concerning the metals: Ag, Pb, Ni, Sn, Cd which have been investigated in this first part of our systematic experimental research.

Silver

While research work on hydrogen overvoltage on silver electrodes are very numerous (1, 6, 7, 8, 9, 10), results of different authors are not always in agreement.

Loshkarev and Ozerof (7) obtained for the Tafel slope of finely subdivided silver the value of 60 mV; and Hillson (10) obtained the same value for silver in aqueous solution of hydrogen chloride.

Using a more accurate experimental technique, Bockris and coworkers (11, 12, 13, 14) observed that the Tafel line has two different slopes for silver electrodes, the first with b values of the same order as that observed by the preceeding authors (60-70 mV), the second one with greater value (120 mV). Moreover they found that overvoltage varies with acid concentration and that the stoichiometric number has a value of about the unity.

Theoretical interpretations of experimental data are also discordant, although according to recent work (8, 13, 14, 15, 16, 17) the rate-determining step of the kinetics of hydrogen evolution for silver is an electrochemical one in the low current density region, and a mixed one (low discharge and electrochemical desorption) for higher current density regions.

Lead

Hydrogen overvoltage studies on lead have been generally restricted to aqueous solutions of acids giving insoluble salts, as hydrochloric acid, sulfuric acid and mixtures with potassium iodide (1, 18, 19, 20, 21, 22, 23, 24).

Kabanov and Jofa (20) using an accurate experimental technique, found that in the low c. d. range $(10^{-3}$ to 10 A/m$^2)$ the Tafel line slope is of the same order as that found for other metals (120 mV).

Bune and Kolotyrkin (23) obtained the same results for hydrochloric acid, for sulfuric acid and its mixture with potassium iodide, the Tafel law being followed while the slope value was 120 mV.

But at the c. d. value for which the overvoltage value reached the so-called "zero charge potential" of the metal, they found a rapid rise of the overvoltage followed by a linear overvoltage vs. log. c. d. relation, with the same slope as before. They attribute the first Tafel line, that at low current density (different for the different solutions) to hydrogen evolution on the metal surface covered with adsorbed ions, while the second one, at higher c. d. common for the different solutions, to the hydrogen evolution on the free lead surface.

The Tafel law is followed also for porous lead electrodes (24) in about 5 M sulfuric acid solutions between 10 and 10^4 A/m^2.

Porous lead electrodes are less sensitive to poisoning than smooth electrodes; the observed hydrogen overvoltage values are characterized by their stability and are easily reproducible.

Recently Mituya and Yamazaki found that in the very low c. d. range (between 10^{-6} and 10^{-2} A/m$^2)$ in 0. 1 M HCl solution the dependance overvoltage vs. log c. d. is not linear (25).

Nickel

Owing to the interest which nickel presents, hydrogen overvoltage measurements on polycrystalline electrodes are very numerous.

We shall consider only some recent selected work, as that of Bockris and Potter (26), to which one may refer for previously published work.

By careful purification (pre-electrolysis), Tafel lines were observed for both acid (HCl) and alkaline (NaOH) solutions of different concentrations

and at different temperatures, the b values not exceeding 125 mV.

According to the interpretation advanced by the quoted author the rate determining step of the hydrogen evolution reaction is the slow discharge, followed by a recombination step involving adsorbed hydrogen atoms (27). The discharge probably occurs from hydroxonium ions in acid solutions and from water molecules in alkaline ones (28).

However more recently, considering the behavior of the heat of adsorption for several metals including nickel, Bockris and Conway (29) maintained that the rate determining process in acid solutions must be the electrochemical one, in opposition to what above stated and the problem is not yet resolved.

The hydrogen overvoltage at electro-deposited nickel cathodes, in aqueous hydrochloric acid solutions (0, 01 - 0, 5 M), has been investigated by Ammar and Award (30).

The Tafel line is broken presenting two branches: that in the low c. d. range having a value of about 60 mV, the second one, at the higher c. d. , a b value of about 110 mV.

The differences between their results on electroplated nickel and those on massive nickel may be attributed to the smaller hydrogen surface coverage at the start of the measurements for electrodeposited cathodes.

In this case desorption processes have been considered rate determining: yet the smaller slope cannot be explained on the basis of either a single electrochemical or a single catalytic desorption mechanism, but may be accounted for by an electrochemical-catalytic mechanism. On the other hand, electroplated nickel in alkaline solutions (31) exhibits the same behavior as massive nickel, so that the mechanism is maintained to be the same. Overvoltage values at a constant c. d. are numerically lower, because of the different true surface areas.

In very concentrated alkaline solutions (7, 9 M KOH) and for high c. d. values (more than 10^3 A/m^2), nickel electrodes present hysteresis

phenomena: overvoltage values for increasing c.d. being higher than for decreasing ones (32).

Some papers on hydrogen overvoltage on nickel alloys with the following metals: iron (33), cobalt (34), copper (35), zinc (36), palladium (37), tin (38) have been recently published. Recently a great interest has also arisen, particularly among Russian authors, on the changes in hydrogen overvoltage caused by the presence of some additions in the solutions or in the electrode.

Tin

Research studies on hydrogen overvoltage on tin electrodes are few in number and the agreement between the results of different authors is by no means satisfactory.

The results of Hickling and Salt and the subsequent ones of Pecharskaya and Stender have yet been discussed.

The b value obtained by the first authors from the slope of the curve at the lowest c.d., before the maximum value, amounts to about 200 mV (1), that by the last two to 130 mV (3).

Rise of temperature causes a substantial diminution in overvoltage, corresponding to an average temperature coefficient of approximately -2 mV/°C (39).

In alkaline solutions (6 M NaOH), on the contrary the dependence law is a linear one, between 10 and 10^4 A/m^2; but b values are about 230 mV (5).

Moreover for a tin cathode in water and organic solvent mixtures (ethyl alcohol, dioxan), the hydrogen overpotential is lower than in aqueous solution at ordinary temperatures in the same c.d. range and maxima are reached at intermediate compositions (40).

Recently Ammar and Sabry (41) measured hydrogen overpotentials on electroplated tin and on copper-tin alloys in M HCl solutions at 30°C in the

low c. d. range (between 0. 1 and 10^2 A/m^2) and their results will be subsequently compared with ours.

Cadmium

The behavior in the high c. d. range has been examinated above.

Instead Kolotyrkin and Medvedeva (22) working in a low c. d. range (between 0. 01 and 10 A/m^2) encountered in 0, 65 M H_2SO_4 an upward overvoltage shift from - 0. 75 V to - 0. 92 V at c. d. of about 1 A/m^2; while on either side of the shift the plot overvoltage vs. c. d. followed Tafel's equation with a slope of about 120 mV.

The authors give evidence that the shift appeared for an overvoltage value corresponding to the zero charge of the surface, and that the two branches referred to differently charged surfaces.

Indeed the upper branch was independent of the nature of the anion (the position remaining practically the same in 0. 65 M H_2SO_4 and in 1. 15 M HCl), while, on the contrary, the lower branch, lay distinctly higher in HCl than in H_2SO_4.

The influence of the concentration of the same acid (0. 05, 0. 85 and 5 M H_2SO_4) was different on the two branches. At high c. d. , overvoltage depended on the concentration of the acid only above 0. 5 M whereas at lower c. d. , overvoltage depended on the concentration only below 0. 5 M and was independent of it at higher acid concentration.

As a consequence of this behavior, Cd electrodes in 0. 05 M H_2SO_4 did not present the shift.

E. Albrecht (42) determined hydrogen overvoltage on (0001) oriented Cd electrode in 0. 5 M H_2SO_4, between 10 and 300 A/m^2.

He found two Tafel lines, shifted one from the other about 100 mV, while polycrystalline cadmium had about an intermediate position, but with a smaller slope (80 mV than 130 mV).

In table I are reported for comparison numerical values obtained from the above mentioned different authors.

The results, as stated, are not in agreement, but could be divided into two classes, according to the range of overvoltage values.

The Tafel law holds also for alkaline solutions (0.2 to 15.4 M KOH; 0.6 M NaOH and 6 M NaOH), (5, 43, 44, 47). Also in this case, while the values of b determined by the different authors are nearly the same, the values of a vary over a wide range.

Examples are reported in table I.

Conclusion

The review above, which shows the lack of agreement on many essential phenomenological aspects, and the practical absence of any research work on the behavior of single crystal electrodes, is sufficient to indicate the need of new systematic work.

TABLE I

Authors	Orientation	Solution	b (mV)	Overvoltage at	
				1 A/m² (mV)	10 A/m² (mV)
Pecherskaya-Stender (3)	Polycryst. Cd	1 M H_2SO_4	210	-	510
Albrecht (42)	Polycryst. Cd	0,5 M H_2SO_4	76	-	550
	(0001) Cd'	0,5 M H_2SO_4	130	-	500-580
Sergeev (45)	Polycryst. Cd	H_2SO_4	-	360	570
Hickling - Salt (1)	Polycryst. Cd	1 M HCl	250	-	990
Ammar - Hassanein (47)	Polycryst. Cd	0,01 M HCl	180	900	1080
Kolotyrkin - Medvedeva (22)	Polycryst. Cd	0,05 M H_2SO_4	120	900	1020
		0,65 M H_2SO_4	120	shift	1020
Belmondi (46)	Polycryst. Cd	1 M HCl	137	980	1115
		0,5 M H_2SO_4	137	1245	1380
		1 M $HClO_4$	144	1318	1460
This work	Polycryst. Cd	0,02 M $HClO_4$	150	635	790
Ammar - Hassanein (47)	Polycryst. Cd	0,01 M NaOH	170	600	-
Zholuder - Stender (5)	Polycryst. Cd	6 M NaOH	160	-	580
Jofa - Braun (43)	Polycryst. Cd	6 M KOH	135	-	915
Genta - Belmondi (44)	Polycryst. Cd	6 M KOH	110	1365	1475

II. Experimental technique

The perchloric acid and hydrochloric acid used for the measurements were pure Merck products.

Sulfamic acid was a pure commercial product, three times recrystallized, to avoid sulphate presence.

The water used for preparing the solution was twice distilled in a glass apparatus.

The solutions used for the overvoltage measurements were pre-electrolysed at a c.d. indicated in table II for the different metals using a cathode of platinum and an anode of platinized platinum (48).

The technique for the preparation (by a modified Bridgman method) of single crystals, their orientation, cutting (by a chemical and electrochemical method avoiding stresses), has been previously described (49, 50).

The conditions of the finishing for the different metals are also reported in table II.

With one exception (lead) the surfaces have been electropolished.

In some cases, that is for nickel and cadmium electrodes, the electrodes were successively treated as cathodes in a fresh solution of the same composition to develop hydrogen on the surface.

The electropolished electrodes were then dried with nitrogen and put into the measurement cell, where sometimes it followed a pre-polarisation in pre-electrolyzed measurements solution, for 3-4 hours at 15 A/m^2 for Ni and Cd electrodes and at 1,5 A/m^2 for Pb.

Fig. 1 shows the apparatus arrangement suitable for hydrogen overvoltage measurements.

Hydrogen, purified from oxygen traces by a palladium catalyst, passes through a concentrated sulfuric acid trap A, through a twice distilled water trap B and finally enters the electrolytic cell.

TABLE II

| Electrode	Electrode polishing	Pre-polarisation of the electrode in the measurements cell	Pre-electrolysis conditions of the solution
Ag	5 % KCN (2-3 V)	none	15 - 20 Coul/cc at 0, 3 - 0, 4 A
Pb	80 parts CH_3COOH and 20 parts 35% H_2O_2	3 - 4 hours at 1, 5 A/m^2	the same
Ni	70% H_2SO_4 (60 V), followed by cathodic treatment	3 - 4 hours at 15 A/m^2	50 - 60 Coul/cc at 0. 05 A
Sn	$HClO_4$ d = 1, 54 (50 V)	none	the same
Cd	45% H_3PO_4 (2 V) followed by cathodic treatment	3 - 4 hours at 15 A/m^2	the same
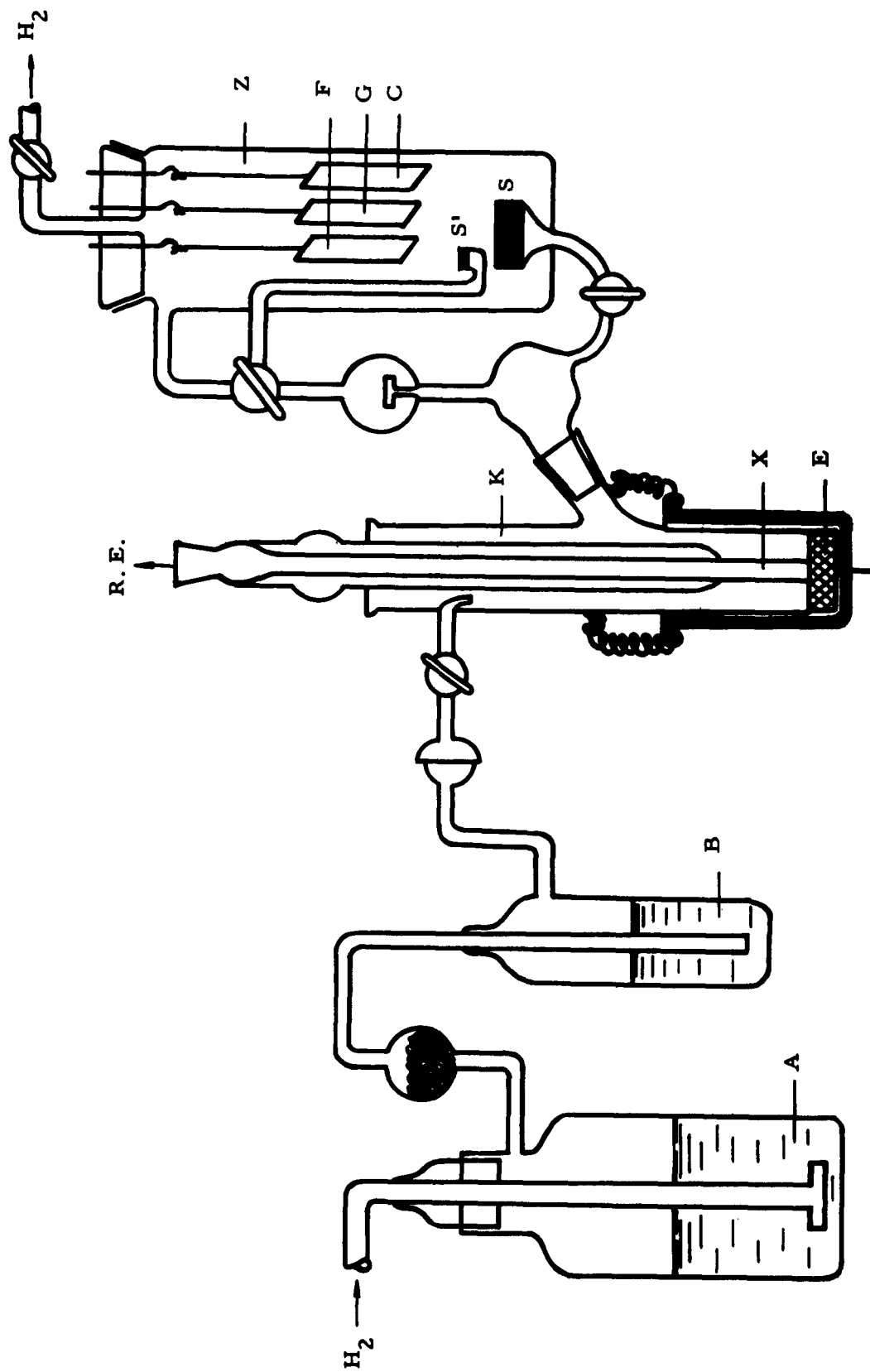
Fig. 1 - Apparatus arrangement for hydrogen overvoltage measurements.

This consists of two parts: K the cathodic compartment and Z the anodic one. In this last, solution purification is made by a pre-electrolysis with hydrogen saturated platinum electrodes F and G; hydrogen entering through the sintered glass disk S (51).

During hydrogen overvoltage measurements, to mantain liquid connection between cathode E and anode C (platinized platinum), hydrogen passes through the sintered glass disk S'.

E is connected with the reference electrode R. E. through the probe X.

As stated, the anode consists during the pre-electrolysis or measurements of a platinized platinum net with a great surface. In our conditions, (hydrogen atmosphere and small current intensity particularly during overvoltage measurements), the anodic reaction was the hydrogen oxydation process and not the oxygen evolution.

So, after the 3-4 hours that hydrogen passed through the apparatus, oxygen was completely eliminated and no other oxygen was formed during the subsequent measurements.

As reference electrodes: Hg/Hg_2SO_4 0.1 M H_2SO_{4aq} electrode for perchloric acid solutions, and Hg/Hg_2Cl_2 0.1 M HCl_{aq} for hydrochloric acid solutions have been utilized.

In an other cell (Fig. 2) the e. m. f. has been determined for the chain formed by the reference electrodes above and a reversible hydrogen electrode of platinized platinum P, the solution and temperatures used being the same as the overvoltage measurements [x].

So, as usual, we adopted as absolute overvoltage values, the absolute values of the difference between the voltages relative to the reference electrode: of the polarized electrode and of the reversible hydrogen electrode.

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[x] For silver electrode this value was calculated, since no junction potential is involved (52).

The overvoltage measurements were carried out supplying the cell
with current and recording the voltage response of the tensiometric
element by means of a Leeds and Northrups recording potentiometer for
the medium rate or slow phenomena and sometimes, by means of a
Tektronix oscilloscope for the quick processes.

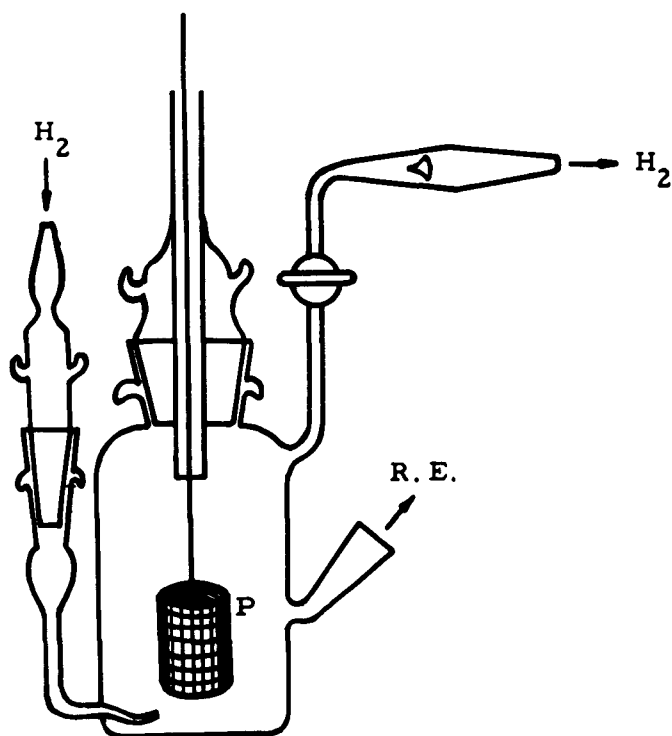Measurements have been made by increasing and decreasing c. d.

Fig. 2

III. Overvoltage measurements

In all cases examined, sometimes only for a small c. d. range as for nickel SCE, the Tafel law is followed, that is: $|\Delta \ell| = a + b \log i$ or the absolute overvoltage value $|\Delta \ell|$ is a linear function of the logarithm of c. d. for the hydrogen evolution reaction.

Table III gives a comparison of the results obtained for the different SCE in the different solutions, as far as the orientation, temperature, acid concentration and anion influence on hydrogen overvoltage is concerned. A more detailed analysis is reported for each metal in the following pages.

Silver

The results concerning hydrogen overvoltage measurements on silver SCE and polycrystalline silver electrodes in sulfuric acid solutions are given in detail in Technical Note Nr.* and in the paper (53) and are summarized as stated above in Table III.

For silver electrodes there are two Tafel slopes, the first one having the smallest value (Fig.3) (see T. N.*).

It may be interesting to examine the behavior of (110) Ag SCE in greater detail.

In most cases there are two branches as found for the other electrodes, but sometimes the difference between their slopes is so small, thet they are nearly coincident and we find only one (the smaller one), as shown in Fig. 5 (see T. N.*).

Tables IV and V (see T. N.*) give the numerical values obtained for the Tafel constants a and b for the examined electrodes in the different experimental conditions.

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Electrode	Solution	Orientation influence (at 25°C)	Temperature influence	Acid concentration influence	Anion influence (at 25°C)
Ag	0.1 M H_2SO_4	none	regular	-	-
Pb	dilute $HClO_4$	(110)>(111)>(100)	regular	regular	$HClO_4 > H_2N - SO_3H$
	dilute H_2N-SO_3H	(100)>(111)>(110)	regular	regular	
Ni	0.150 M $HClO_4$	(110)≩(111)>(100)	regular	-	$HCl>HClO_4>H_2N-SO_3H$ for (110) and (111) Ni
	0.005 M HCl	(110)>(100)>(111)	regular	-	$HCl>HClO_4$ only for
	0.105 M H_2N-SO_3H	(110)>(100); (111) Ni exceptional	regular	-	low c.d. values.
Sn	0.01 M - 0.08M $HClO_4$	(100)>(110)≩(001)	regular	regular	$HCl>HClO_4$ for(110)Ni;
	0.03 M HCl	(110)>(100)>(001)	regular	-	for (100) and (111) Ni the opposite
Cd	0.005 M $HClO_4$	(10$\bar{1}$0)>(11$\bar{2}$0)>(0001)	regular	regular only for (10$\bar{1}$0) and (11$\bar{2}$0) Cd	-
	0.020 or 0.035 M$HClO_4$	(0001)>(10$\bar{1}$0)>(11$\bar{2}$0)	regular		

Lead

The results concerning the hydrogen overvoltage measurements on lead SCE and on polycrystalline lead electrodes in perchloric acid and in sulfamic acid solutions, are given in detail in Technical Note Nr.[*] and in the paper (54) and are resumed in Table III.

The Tafel law is followed but in many cases there are two different slopes; that in the lower c. d. range being now the highest one (Fig. 6, 7 and 8) (see T. N.[*]).

Hysteresis phenomena are observed in concentrated perchloric acid solutions (about 0, 08 M) in the lower c. d. range, these are not due to surface conditions not to traces of depolarized or inhibiting substances, the values obtaines for increasing c. d. being always higher than those by decreasing c. d.

The hysteresis decreases with increasing temperature and by repeating measurements.

In this case, however, while the diagrams for polycrystalline and (110) SCE have the usual form with a smaller second slope, the second slope for (100) and (111) SCE is greater (Fig. 9) (see T. N.[*]).

For sulfamic acid solutions, by increasing the acid concentration, the second branch with the smaller slope is shifted towards higher c. d. values and sometimes beyond the accessible range of c. d. (Fig. 8) (see T. N.[*]).

Behavior in dilute perchloric acid solution, acid concentration influence on (100) Pb SCE and anion influence on polycrystalline lead are shown respectively in Fig. 10, 11 and 12 (see T. N.[*]).

In tables VI to IX the experimental results are reported as far as the values are concerned of: b, of the exchange c. d. (i_o), and of the intersection coordinates of the two Tafel straight lines under the different experimental conditions.

[*]WADC Technical Note 59-393

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Nickel

The results concerning the hydrogen overvoltage measurements on nickel SCE in perchloric acid, hydrochloric acid and sulfamic acid solutions, are given in detail in Technical Note Nr.*, in the paper (55) and in table III..

The Tafel law holds only in a small c.d. range, with one slope (Fig.13, see T. N.*).

While nickel electrodes are slightly attacked in hydrochloric acid solutions so that the least overvoltage values are more cathodic than the reversible hydrogen overvoltage value, they behave in the other acid solutions as noncorroding electrodes (Fig.14, see T.N.*).

The temperature influence on the behavior of Ni SCE in perchloric acid solutions is shown in Fig.15, 16 and 17 (see T. N.*), respectively at 25, 45 and 65°C.

As the figures show, the difference between the overvoltage values of the (110) and (111) oriented SCE increases with increasing temperature, at 25°C these values being nearly coincident.

The behavior in hydrochloric acid solutions is reported on Fig. 18 (see T. N.*) together with Bockris' results on massive nickel (B) (26) and Ammar's on electroplated electrodes (E) (30) in 0,01 M HCl solution. The agreement is good.

In sulfamic acid solutions the behavior of (111) SCE could be considered exceptional (Fig. 19).

The initial overvoltage values are sometimes to large; in this case subjecting the electrode to a high c. d. for some time (for example at 40 A/m^2, for 1 ($\overrightarrow{b}$) to 3 ($\overrightarrow{a}$) hours), the values decrease ($\overleftarrow{b}$ and $\overleftarrow{a}$), and approach a limit (c), whose parameters are given in table XII (see T. N.*).

Leaving the electrode overnight in the solution, the successively measured overvoltage values are a little increased, the b values being the same, however. This behavior may be attributed to hydrogen saturation of the surface or to residual oxide present on the surface, which for (111)

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SCE is not eliminated by preliminar treatments.

In tables X to XII (see T. N. [*]) experimental results are reported as far as the values are concerned of: a and b, of the exchange c. d. i_o, of the overvoltage at two different c. d. (at 0. 1 and 10 A/m^2) and of the standard heat of activation of the hydrogen evolution reaction $\triangle H$ (26), for Ni SCE in different experimental conditions.

Tin

The results concerning the hydrogen overvoltage measurements on tin SCE and on polycrystalline electrodes in perchloric acid and in hydrochloric acid solutions are given in detail in Technical Note Nr.[**]in the paper (56) and are resumed in Table III..

The Tafel law is regularly followed in the range explored (between 0. 05 and 10 A/m^2), with one branch, as results from Fig.20 and 21 (see T. N.[**]).

Behavior in 0. 01 M perchloric acid solutions and in 0. 03 M hydrochloric acid solutions are shown respectively in Fig.22 and 23(see T. N.[**]), while acid concentration influence and anion influence are shown in Fig.24 and 25 (see T. N.[**]).

Numerical values are reported in Tables XIII to XVI (see T. N.[*]) for the different cases studied.

The results of Ammar and Sabry (41) are in rather good agreement with those of the present research. Although the values of b (about 110 mV), for electroplated electrodes agree with those obtained for massive electrodes the overvoltage results are numerically smaller than ours, perhaps due to the larger surface area (that is to a smaller true c. d. for electroplated electrodes as compared to ours).

Cadmium

The results concerning the hydrogen overvoltage measurements on cadmium SCE and on polycrystalline electrodes in perchloric acid solutions are given in detail in Technical Note Nr.* , in the paper (57) and in Table III.

Fig.26 and 27(see T.N.*) demonstrate the validity of Tafel law with one slope for cadmium electrodes in a wide c.d. range and Fig.28 (see T.N.*) shows the dependence law of overvoltage values upon time at constant c.d. obtained by oscillographic recording for (0001) SCE.

An interesting remark should be made for cadmium electrodes relative to the acid concentration influence: indeed increasing acid concentration, overvoltage values decrease for $(10\bar{1}0)$ and $(11\bar{2}0)$ Cd, where they increase for polycrystalline Cd and to a greater extend for (0001) Cd (Fig. 29).

This influence is so strong to be able to change the orientation influence on overvoltage values in respect to dilute solutions (Fig.30 (see T.N. *).

In fact the (0001) SCE, which is the most densely packed one, has the lowest overvoltage values in dilute solutions, but has the highest ones in concentrated solutions.

In Table XVII to XX (see T.N.*) experimental numerical values for the different electrodes are reported.

Comparing our results with those of the preceeding studies (see Table I), we could observe:

a) there is no overvoltage shift, maybe because the solutions are very dilute compared to those used by Kolotyrkin and Medvedeva (22), as found also by Belmondi (46) for 1 M $HClO_4$ solutions;

b) the overvoltage and b values are intermediate between those obtained by the other authors.

A detailed discussion of the theoretical aspects of the results above will be postponed after completion of the experimental work now carried out in this Laboratory.

*WADD Technical Note 60-269

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TABLE IV

Electrode	Solution	Temp.	a_1 (mV)	a_2 (mV)	b_1 (mV)	b_2 (mV)
(100) Ag	$H_2SO_4 \simeq 0.1$ M	25°C	150	170	75	120
(110) Ag	$H_2SO_4 \simeq 0.1$ M	25°C	150	145 x	70	150 x
(111) Ag	$H_2SO_4 \simeq 0.1$ M	25°C	155	175	70	130
Polycryst. Ag	$H_2SO_4 \simeq 0.1$ M	25°C	120	145	60	135

x See text

TABLE V

Electrode	Solution	Temp.	a_1 (mV)	a_2 (mV)	b_1 (mV)	b_2 (mV)
(111) Ag	$H_2SO_4 \simeq 0.1$ M	25°C	155	175	70	130
		35°C	135	150	70	130
		45°C	135	130	65	135
		60° C	115	90	50	150
	$H_2SO_4 \simeq 0.2$ M	25°C	165	165	70	170
		35°C	150	140	65	155
		45°C	140	120	65	155
	$H_2SO_4 \simeq 0.4$ M	25°C	145	140	65	130
		45°C	140	125	55	140

TABLE VI

Electrode: (100) Pb

Solution	Temp. (°C)	b_1 (mV)	b_2 (mV)	$\log i_{0_1}$ (A/m²)	$\log i_{0_2}$ (A/m²)	$-\Delta E$ (mV)	$\log i$ (A/m²)
HClO₄ 0.010 M	25	256±3	148±2	-2.85±0.05	-5.00±0.10	792±12	0.25±0.10
	35	254±4	148±4	-2.70±0.05	-5.30±0.30	801±8	0.35±0.20
	45	247±2	131±2	-2.50±0.05	-5.50±0.10	824±50	0.75±0.05
HClO₄ 0.075 M	20	198	248	-3.00	-2.25	784	0.80
	35	200	240	-2.85	-2.35	746	0.80
	45	203	223	-2.80	-2.45	706	0.75
H₂N-SO₃H 0.015 M	30	217±3	132±2	-3.15±0.05	-4.45±0.05	454±3	-1.00±0.05
	40	207±4	143±3	-2.85±0.05	-3.70±0.05	440±4	-0.70±0.05
	50	218±3	153±3	-2.59±0.05	-3.40±0.15	420±15	-0.70±0.05
H₂N-SO₃H 0.020 M	30	262±2	138±2	-2.55±0.05	-4.00±0.10	435±15	-0.85±0.05
	40	229±5	145±5	-2.60±0.10	-3.65±0.10	420±15	-0.80±0.10
	50	220±5	154±4	-2.55±0.10	-3.30±0.10	400±10	-0.70±0.05

T A B L E   VII

Electrode: (110) Pb

Solution	Temp. (°C)	b_1 (mV)	b_2 (mV)	$\log i_{o_1}$ (A/m²)	$\log i_{o_2}$ (A/m²)	$-\Delta\tilde{\tau}$ (mV)	$\log i$ (A/m²)
HClO$_4$ 0.002M	25	283±10	140±10	-3.30±0.10	-5.70±0.10	705±13	-0.80±0.10
	35	220±10	150±10	-3.50±0.20	-5.10±0.40	688±40	-0.40±0.20
	45	--	170±10	--	-4.00±0.20	--	--
HClO$_4$ 0.050 M	25	320	185	-2.40	-3.95	654	-0.35
H$_2$N-SO$_3$H 0.015 M	25	204±3	130±10	-3.20±0.10	-5.20±0.10	804±30	1.10±0.30
	35	180±2	--	-3.10±0.05	--	--	--
	45	180±2	--	-2.90±0.15	--	--	--
H$_2$N-SO$_3$H 0.025 M	25	170±5	--	-3.25±0.05	--	--	--
	35	170±5	--	-3.05±0.05	--	--	--
	45	173±3	--	-2.90±0.05	--	--	--

T A B L E VIII

Electrode: (111) Pb

Solution	Temp. (°C)	b_1 (mV)	b_2 (mV)	$\log i_{o1}$ (A/m²)	$\log i_{o2}$ (A/m²)²	$-\Delta E$ (mV)	$\log i$ (A/m²)
HClO₄ 0.005 M	25	240±4	116±8	-3.22±0.05	-6.75±0.80	770±10	-0.05±0.15
	35	237±4	116±4	-3.16±0.10	-6.40±0.20	749±6	0.00±0.05
	45	242±4	91±3	-2.65±0.40	-7.95±0.20	752±3	0.15±0.05
HClO₄ 0.085 M	20	190	320	-3.29	-1.80	728	0.5
	35	200	280	-3.03	-2.00	720	0.6
	50	220	260	-2.63	-2.10	736	0.8
H₂N-SO₃H 0.015 M	30	198±2	-	-3.00±0.10	-	-	-
	40	198±3	-	-2.95±0.05	-	-	-
	50	202±2	132±2	-2.70±0.30	-4.40±0.05	645±17	0.50±0.10
H₂N-SO₃H 0.075 M	30	230±10	-	-2.45±0.15	-	-	-
	35	222±2	-	-2.45±0.05	-	-	-
	45	216±4	-	-2.40±0.05	-	-	-

T A B L E   IX

Electrode: Polycrystalline Pb

Solution	Temp. (°C)	b_1 (mV)	b_2 (mV)	$\log i_{o_1}$ (A/m²)	$\log i_{o_2}$ (A/m²)	$-\Delta \mathscr{E}$ (mV)	$\log i$ (A/m²)
HClO₄ 0.010 M	25	220±10	130±10	-4.05±0.05	-6.30±0.30	804±20	-0.35±0.05
	35	290±10	135±5	-2.40±0.40	-5.75±0.30	752±12	-0.30±0.05
	45	305±5	170±10	-2.50±0.05	-4.35±0.20	724±20	-0.15±0.10
HClO₄ 0.075 M	25	243	170	-3.35	-4.40	671	-0.65
	35	260	185	-2.80	-3.75	646	-0.30
	45	305	185	-2.15	-3.75	776	0.35
H₂N-SO₃H 0.010 M	25	180±5	76±5	-3.15±0.05	-8.55±0.05	724±20	0.90±0.05
	35	180±5	80±5	-3.05±0.05	-7.55±0.05	649±20	0.60±0.05
	45	178±3	100±10	-2.85±0.05	-5.70±0.05	605±20	0.55±0.05
H₂N-SO₃H 0.055 M	25	173±4	-	-3.20±0.15	-	-	-
	35	190±4	-	-2.70±0.15	-	-	-
	45	170±2	-	-2.90±0.05	-	-	-

T A B L E   X

Solution	Temp. (°C)	a (mV)	b (mV)	$\log i_o$ (A/m²)	Overvoltage at		ΔH (Kcal)
					0.1 A/m² (mV)	10 A/m² (mV)	
HClO₄ 0.100 M	25	90±10	100±8	-0.85	25	190	5
	45	50±10	80±8	-0.65	5	145	
	65	35±10	75±8	-0.45	-5	110	
HCl 0.003 M	25	195±10	100±5	-2.05	100	290	6
	45	175±10	105±5	-1.80	80	270	
	65	165±10	105±5	-1.70	70	255	
H₂N-SO₃H 0.105M	25	50±4	135±5	-0.40	0	190	12
	35	25±4	150±8	-0.15	-10	175	
	45	-20±4	155±5	+0.15	-15	125	

T A B L E XI

Electrode: (110) Ni

Solution	Temp. (°C)	a (mV)	b (mV)	$\log i_o$ (A/m²)	Overvoltage at 0.1 A/m² (mV)	Overvoltage at 10 A/m² (mV)	$\triangle H$ (Kcal)
$HClO_4$ 0.150 M	25	190±5	155±5	-1.20	55	350	6
	45	155±5	150±5	-1.05	35	325	
	65	120±5	160±5	-0.74	30	280	
HCl 0.005 M	25	245±5	80±5	-3.05	160	325	8
	45	230±5	85±15	-2.70	145	315	
	65	205±5	85±5	-2.40	120	290	
H_2N-SO_3H 0.105 M	25	110±5	130±5	-0.85	30	250	12
	35	105±5	135±5	-0.75	15	240	
	45	55±5	130±5	-0.40	5	185	

TABLE XII

Electrode: (111) Ni

Solution	Temp. (°C)	a (mV)	b(mV)	log i_o (A/m^2)	Overvoltage at		ΔH (Kcal)
					0.1 A/m^2 (mV)	10 A/m^2 (mV)	
HClO$_4$ 0.150 M	25	180±5	150+10	-1.20	60	335	10
	35	160±5	145±10	-1.10	35	305	
	45	120±5	145±10	-0.85	20	265	
	65	75±2	135±5	-0.55	5	210	
HCl 0.005 M.	25	160±5	90±5	-1.80	75	250	10
	45	115±5	105±5	-1.15	30	220	
	65	100±5	90±5	-1.10	20	200	
H$_2$N-SO$_3$H^{x} 0.100M	25	40	90	-0.45	10	130	4
	35	35	80	-0.45	5	115	
	45	25	70	-0.35	0	95	

^{x} See text

T A B L E XIII

Electrode: (001)Sn

Solution	Temp. (°C)	a (mV)	b (mV)	log i_o	Overvoltage at 0.1 A/m² (mV)	Overvoltage at 10 A/m² (mV)	ΔH (Kcal)
HClO$_4$ 0.01 M	30	540±2	105±4	-5,10	435	650	11
	45	525±2	110±2	-4,80	415	635	
	65	495±5	130±2	-3,85	370	625	
HClO$_4$ 0.08 M	25	490±2	120±2	-4,10	370	610	10
	45	450±4	125±4	-3,65	330	565	
	65	400±4	125±4	-3,20	280	520	
HCl 0.03 M	30	485±2	100±6	-4,95	380	580	7
	45	470±2	100±2	-4,70	355	570	
	65	440±2	100±2	-4,35	340	540	

T A B L E XIV

Electrode: (100) Sn

Solution	Temp. (°C)	a (mV)	b (mV)	log i_o (A/m²)	Overvoltage at 0.1 A/m² (mV)	Overvoltage at 10 A/m² (mV)	ΔH (Kcal)
HClO$_4$ 0.01 M	30	600±2	125±4	-4,75	470	725	4
	45	575±4	125±4	-4,60	450	700	
	65	545±2	125±2	-4,40	420	670	
HClO$_4$ 0.08 M	25	550±2	130±2	-4,20	415	680	15
	45	500±4	145±4	-3,45	355	645	
	65	415±4	145±4	-2,85	270	565	
HCl 0.03 M	30	550±4	115±8	-4,80	435	665	9
	45	535±2	120±2	-4,50	410	650	
	65	490±2	125±4	-3,90	350	610	

TABLE XV

Electrode: (110) Sn

Solution	Temp. (°C)	a (mV)	b (mV)	$\log i_o$ (A/m²)	Overvoltage at 0.1 A/m² (mV)	10 A/m² (mV)	$\triangle$H (Kcal)
HClO$_4$ 0.01 M	30	550+4	110+2	-5,00	440	665	10
	45	515+4	105+4	-4,95	415	620	
	65	475+4	115+4	-4,20	360	590	
HClO$_4$ 0.08 M	45	465+4	90+4	-5,05	375	555	-
	65	410+4	90+4	-4,75	320	495	
HCl 0.03 M	25	575+10	115+5	-4,94	460	695	9
	45	560+4	120+4	-4,80	445	680	
	65	525+4	130+4	-4,05	395	655	

TABLE XVI

Electrode: Polycrystalline Sn

Solution	Temp. (°C)	a (mV)	b (mV)	$\log i_o$ (A/m²)	Overvoltage at 0.1 A/m² (mV)	10 A/m² (mV)	$\triangle$H (Kcal)
HClO$_4$ 0.03 M	25	570+4	130+8	-4,30	435	700	9
	45	535+4	135+4	-4,00	402	665	
	65	495+4	140+4	-3,50	355	635	
HCl 0.03 M	25	570+2	120+2	-4,75	430	690	7
	45	555+2	125+2	-4,45	430	675	
	65	525+2	125+2	-4,20	380	645	

T A B L E XVII

Electrode: (0001) Cd

Solution		Temp. (°C)	a (mV)	b (mV)	log i_o (A/m^2)	Overvoltage at		$\triangle$H (Kcal)
						0.1 A/m^2 (mV)	10A/m^2 (mV)	
HClO$_4$	0, 005 M	25	545	135	-4, 05	410	680	-
		40	525	125	-4, 20	400	655	
HClO$_4$	0,020 M	25	665	130	-5, 10	530	790	-
		55	640	110	-5, 80	530	750	

T A B L E XVIII

Electrode: (10$\bar{1}$0) Cd

Solution		Temp. (°C)	a (mV)	b (mV)	log i_o (A/m^2)	Overvoltage at		$\triangle$H (Kcal)
						0.1 A/m^2 (mV)	10 A/m^2 (mV)	
HClO$_4$	0, 005 M	25	630	140	-4, 50	490	770	-
		55	605	130	-4, 65	470	731	
HClO$_4$	0, 020 M	25	610	100	-6, 10	515	710	6
		40	590	100	-5, 90	490	730	
HClO$_4$	0, 035 M	25	610	115	-5, 30	495	725	8
		40	570	115	-5, 00	460	685	

T A B L E   XIX

Electrode: (11$\bar{2}$0) Cd

Solution		Temp. (°C)	a (mV)	b (mV)	log i$_o$ (A/m^2)	Overvoltage at		$\triangle$H (Kcal)
						0.1A/m^2 (mV)	10A/m^2 (mV)	
HClO$_4$	0, 005 M	40	585	100	-5, 85	485	685	6
		55	550	100	-5, 50	450	650	
HClO$_4$	0, 035 M	25	510	110	-4, 65	425	615	
		40	500	110	-4, 55	430	605	-
		55	460	85	-5, 40	405	545	

T A B L E   XX

Electrode: Polycrystalline Cd

Solution		Temp. (°C)	a (mV)	b (mV)	log i$_o$ (A/m^2)	Overvoltage at		$\triangle$H (Kcal)
						0.1 A/m^2 (mV)	10A/m^2 (mV)	
HClO$_4$	0, 005 M	25	565	145	-4, 00	425	705	
		40	545	130	-4, 20	415	675	-
		55	510	130	-3, 90	375	635	
HClO$_4$	0, 020 M	25	635	150	-4, 25	480	790	
		40	610	160	-3, 80	435	770	5
		55	610	160	-3, 85	490	765	
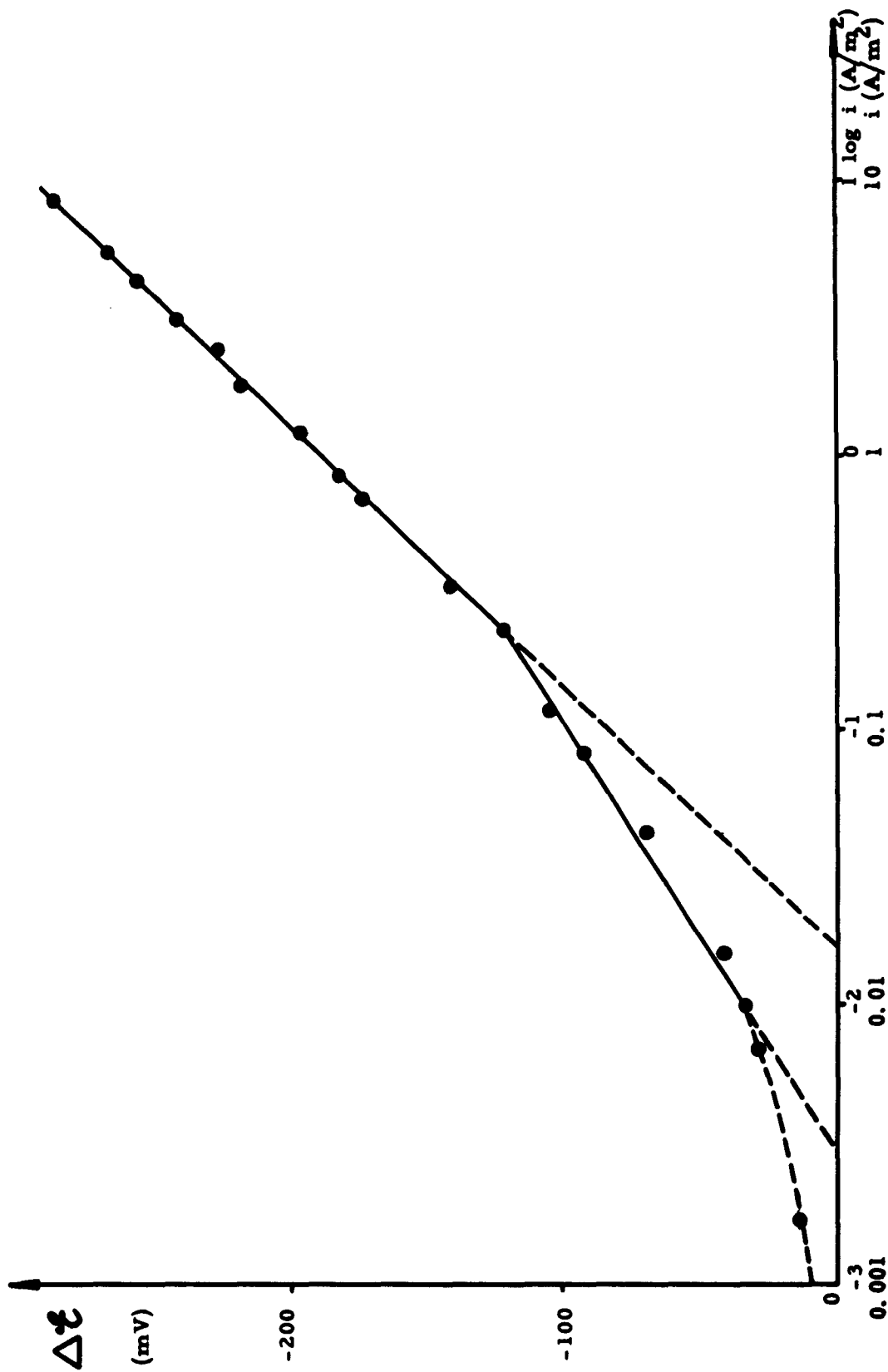
Fig. 3 - (100) Ag/H_2SO_4 0.1 M ; t = 25°C

$\Delta \mathcal{E}$ (mV)

-200

-100

log i (A/m^2)

i (A/m^2)

10

1

0.1

0.01

0.001

-1

-2

-3
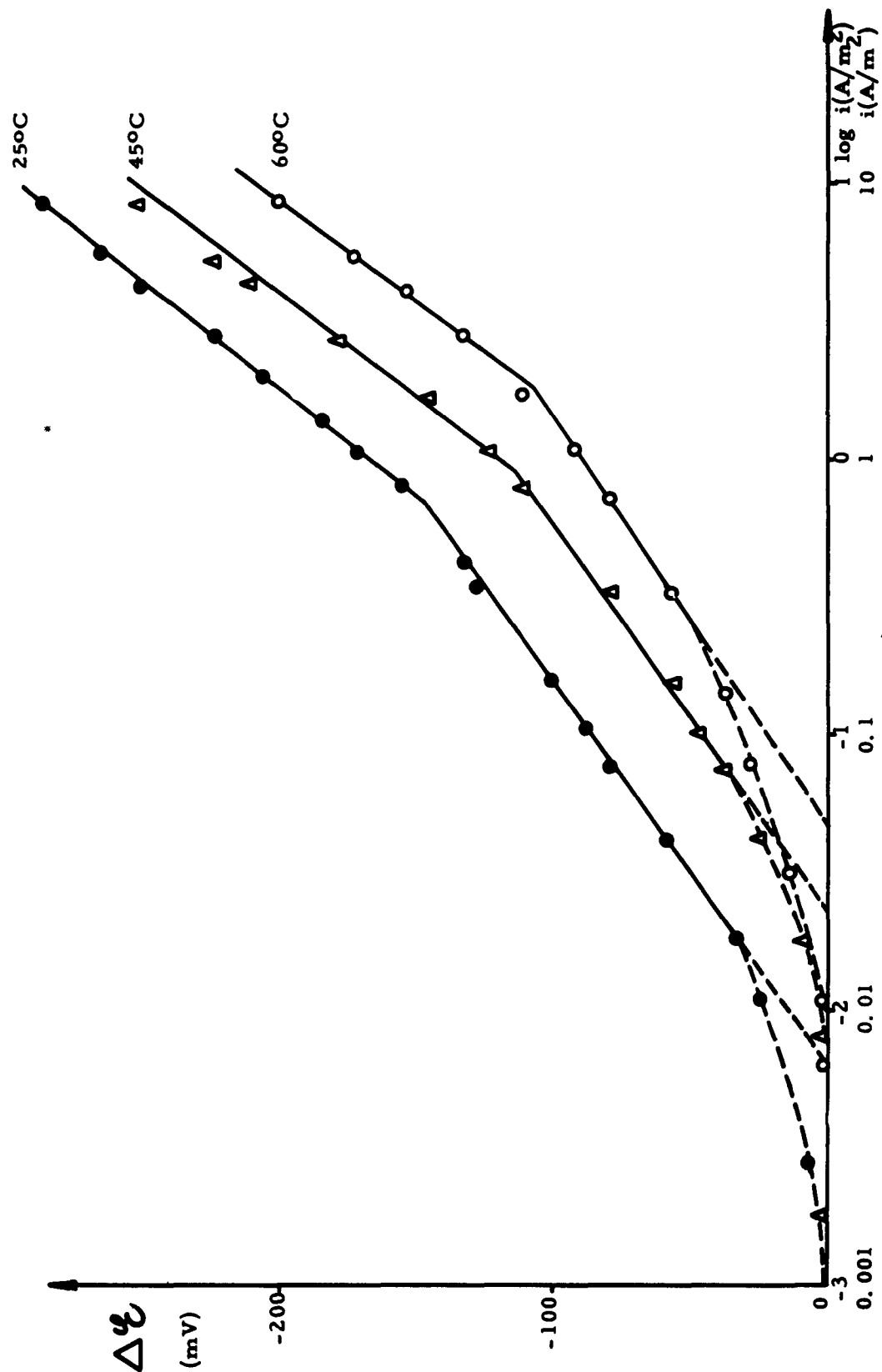
Fig. 4 – (111) Ag/H_2SO_4 0.1M
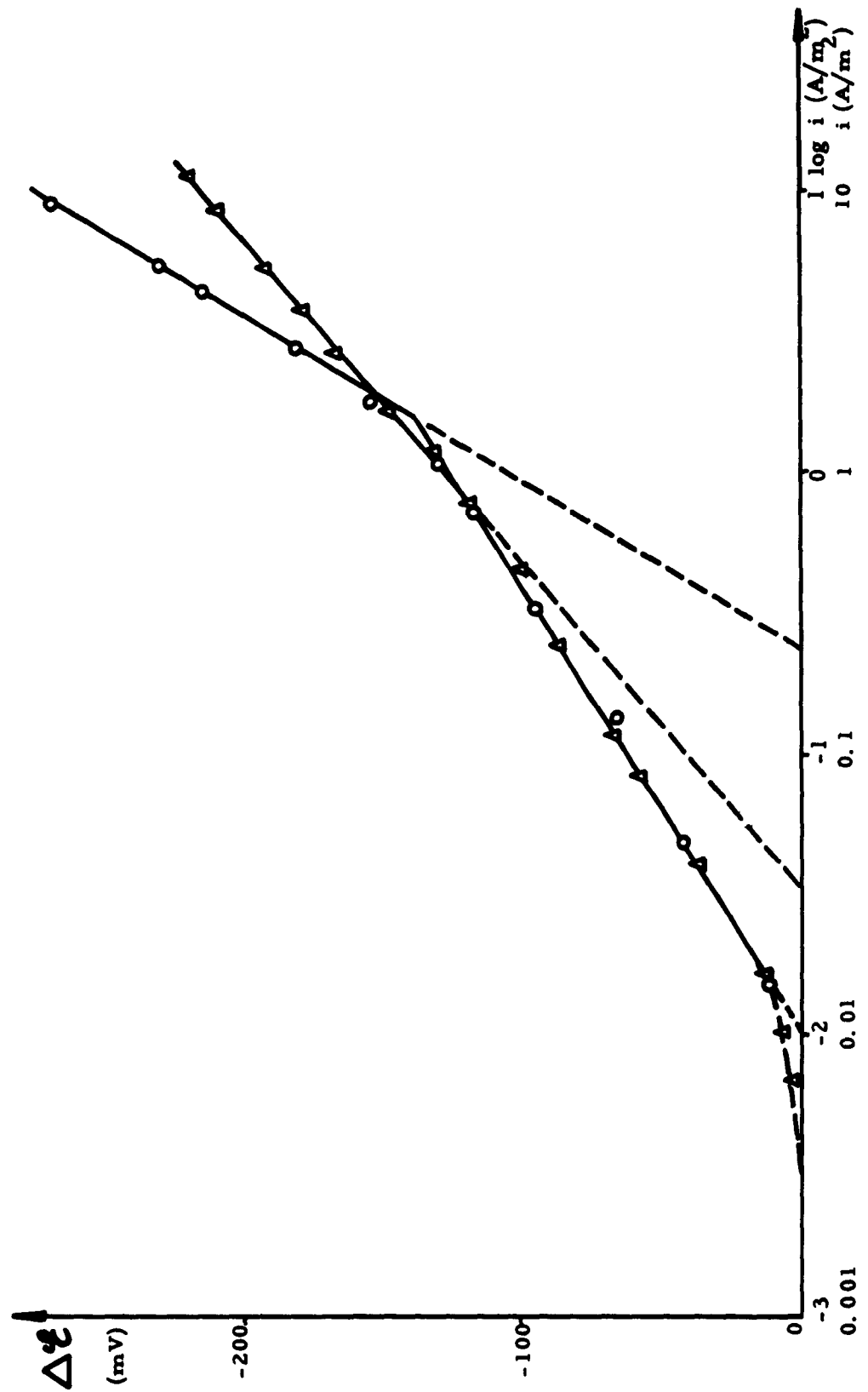
Fig. 5 - (110) Ag/H_2SO_4 0.1 M ; t = 25°C
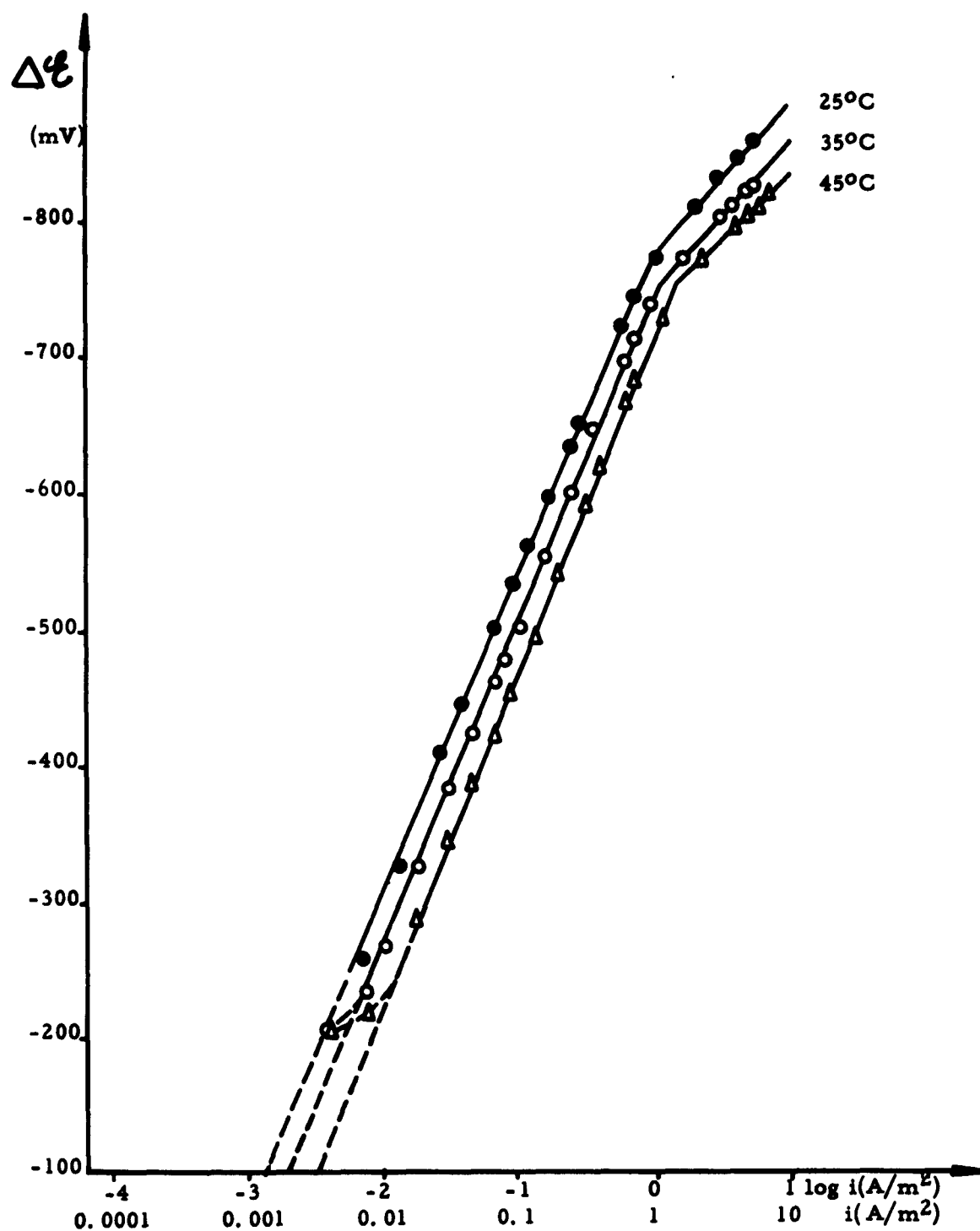
Fig. 6 - (111) Pb/HClO$_4$ 0.007 M
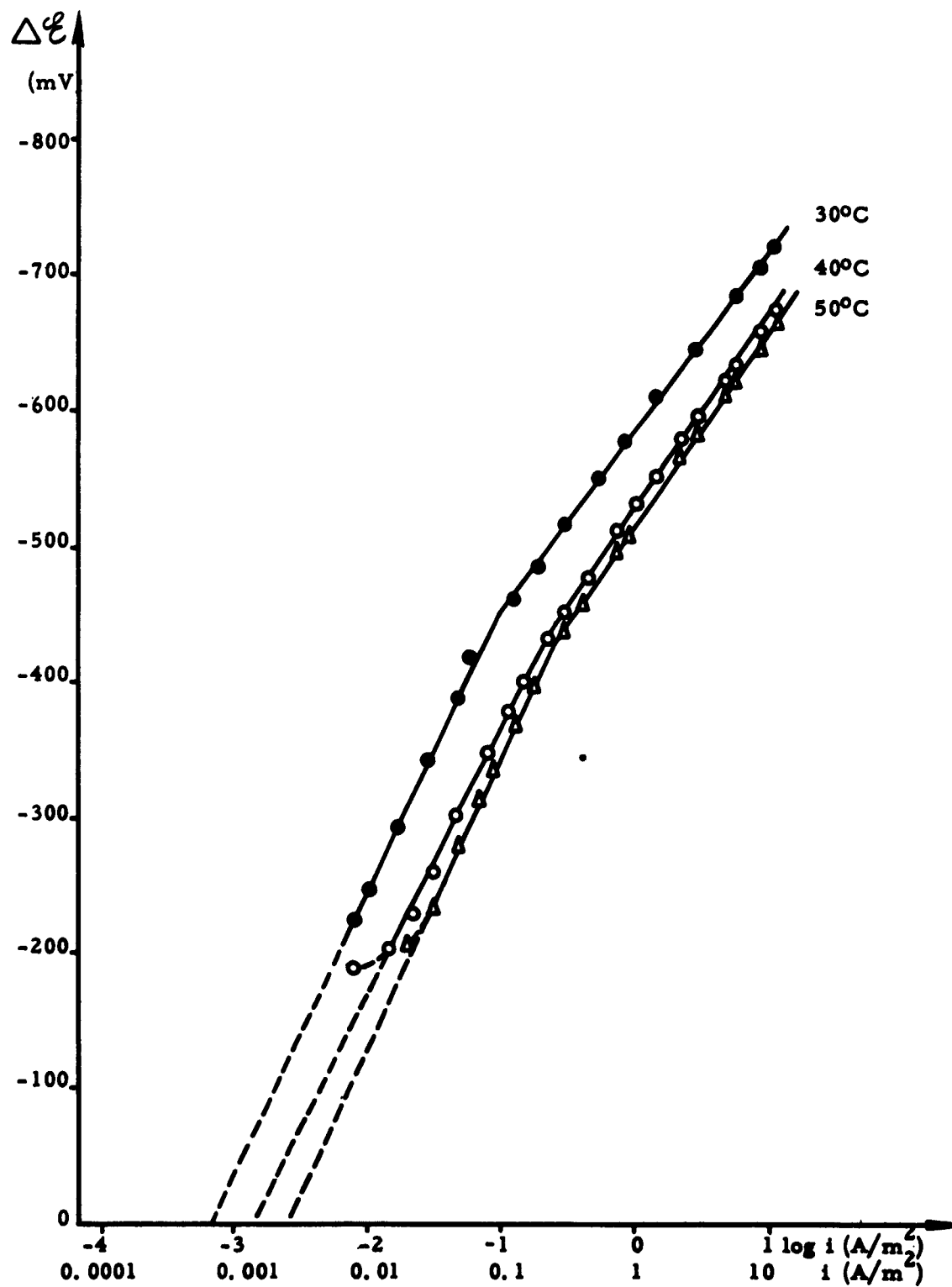
Fig. 7 - (100) Pb/H_2N -SO_3H 0.015 M
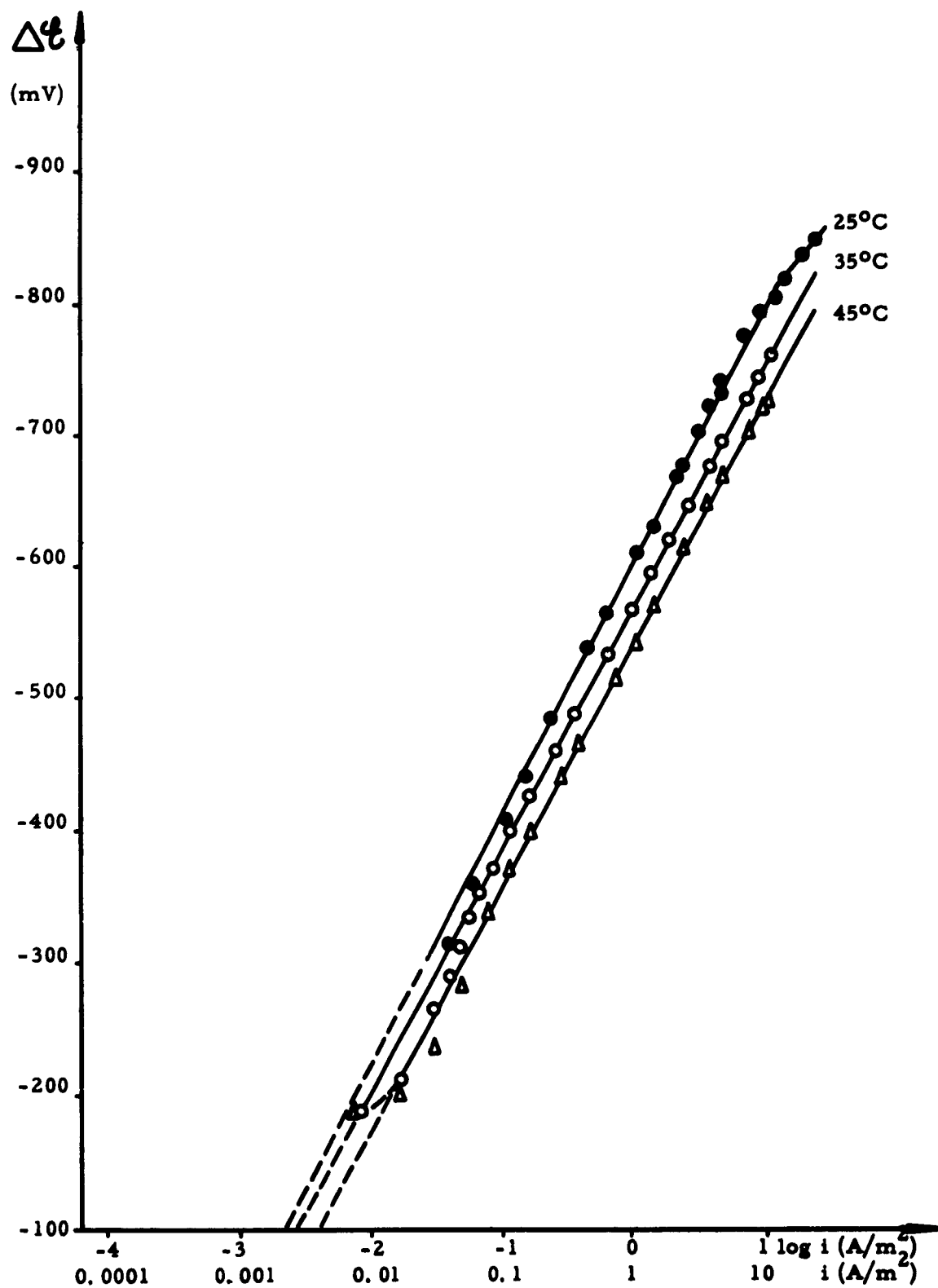
Fig. 8 - (110) Pb/H_2N-SO$_3$H 0.015 M
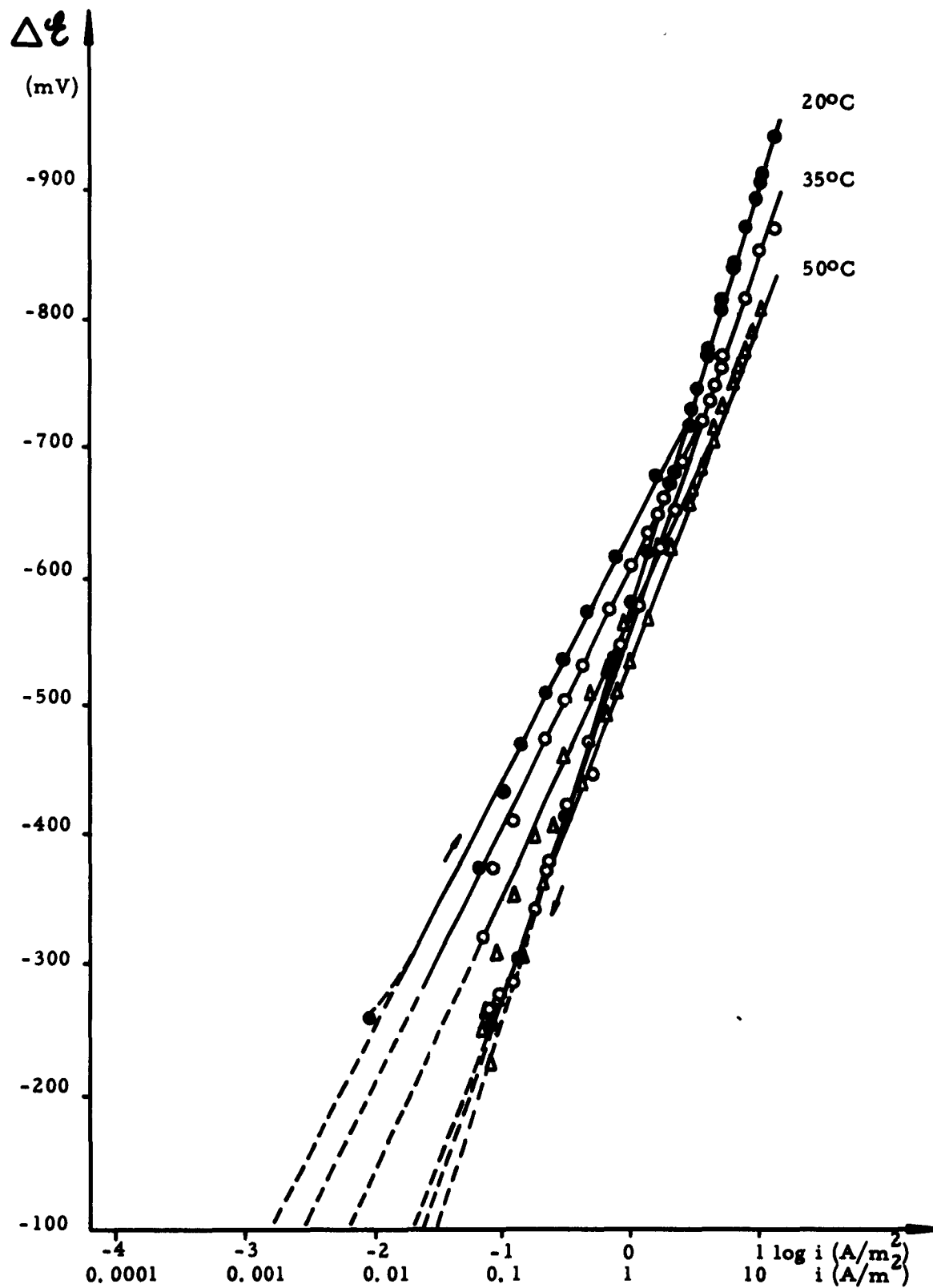
Fig. 9 - (111) Pb/HClO$_4$ 0.085 M
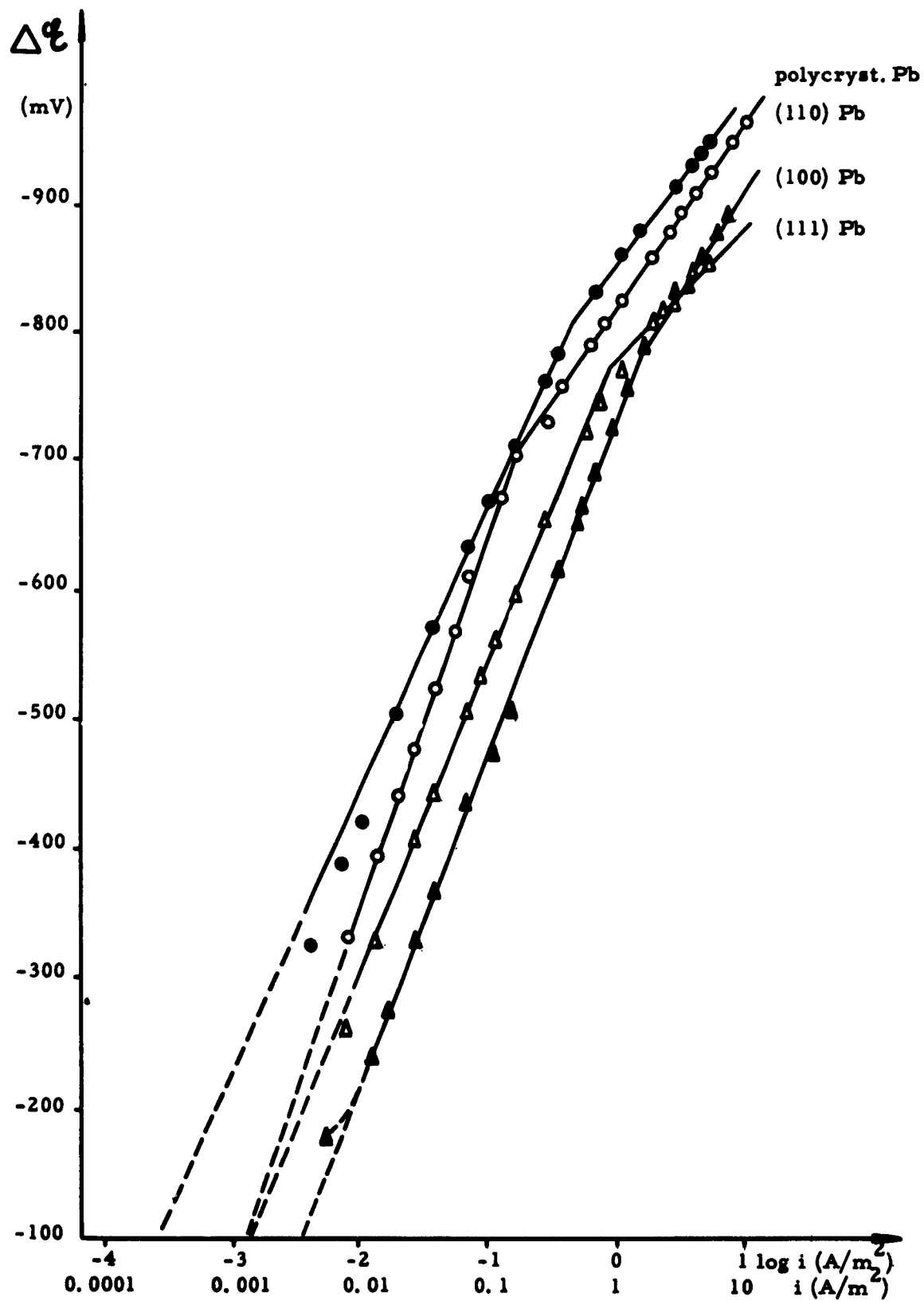
Fig. 10 - Behavior in dilute perchloric acid   t = 25°C
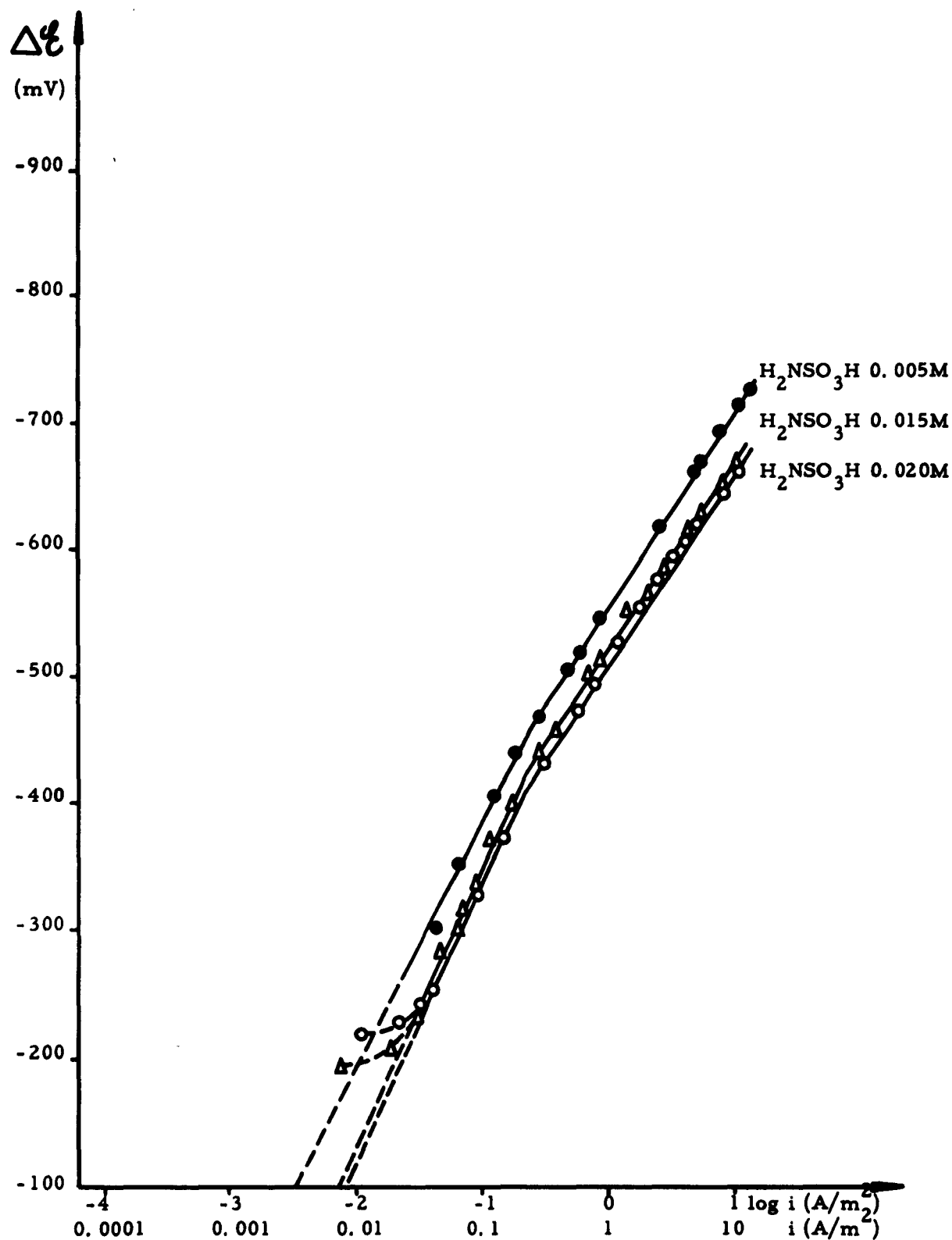
Fig. 11 - (100) Pb   t = 50°C
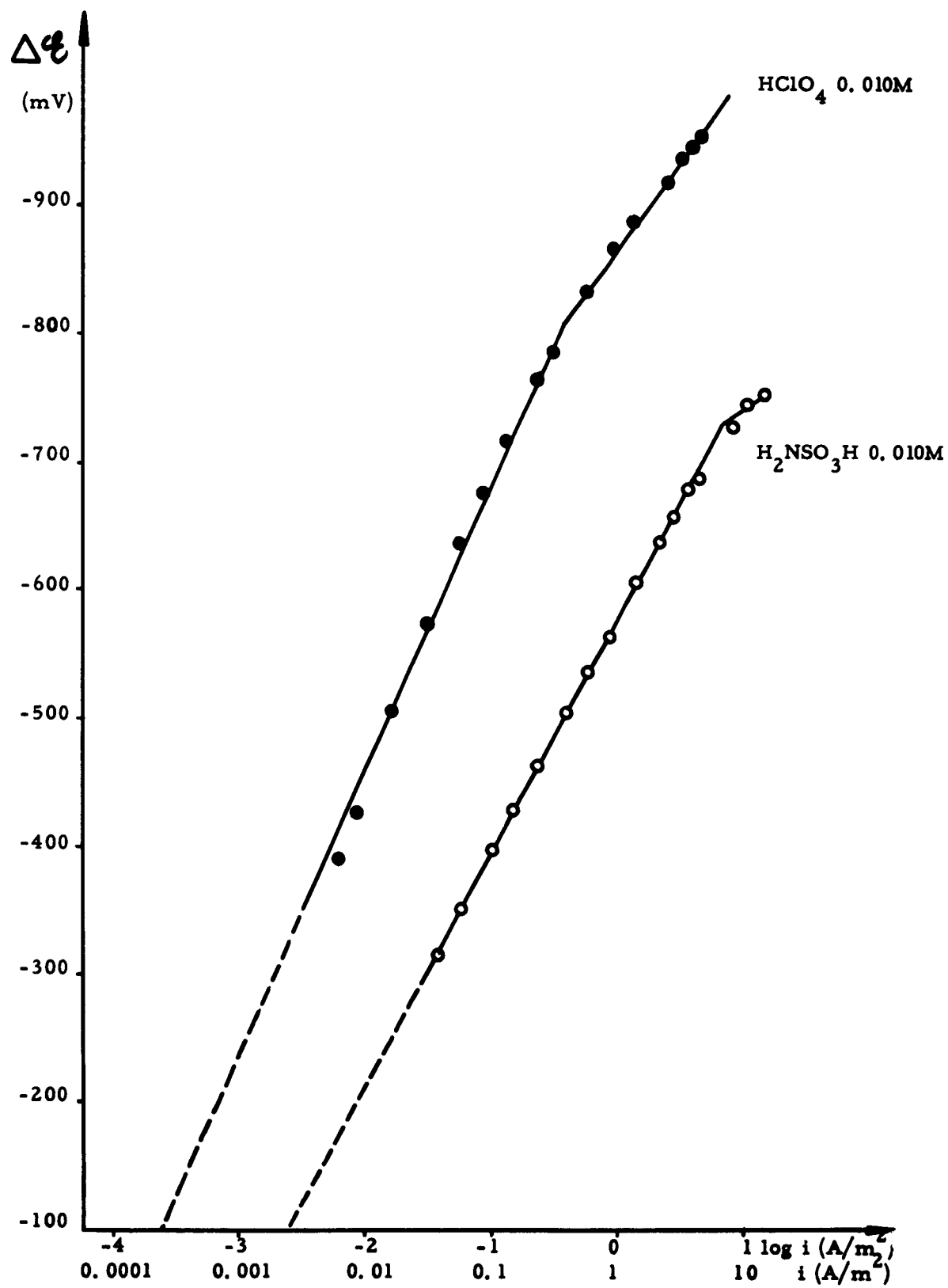
Fig. 12 - Polycrystalline Lead -   t = 25°C
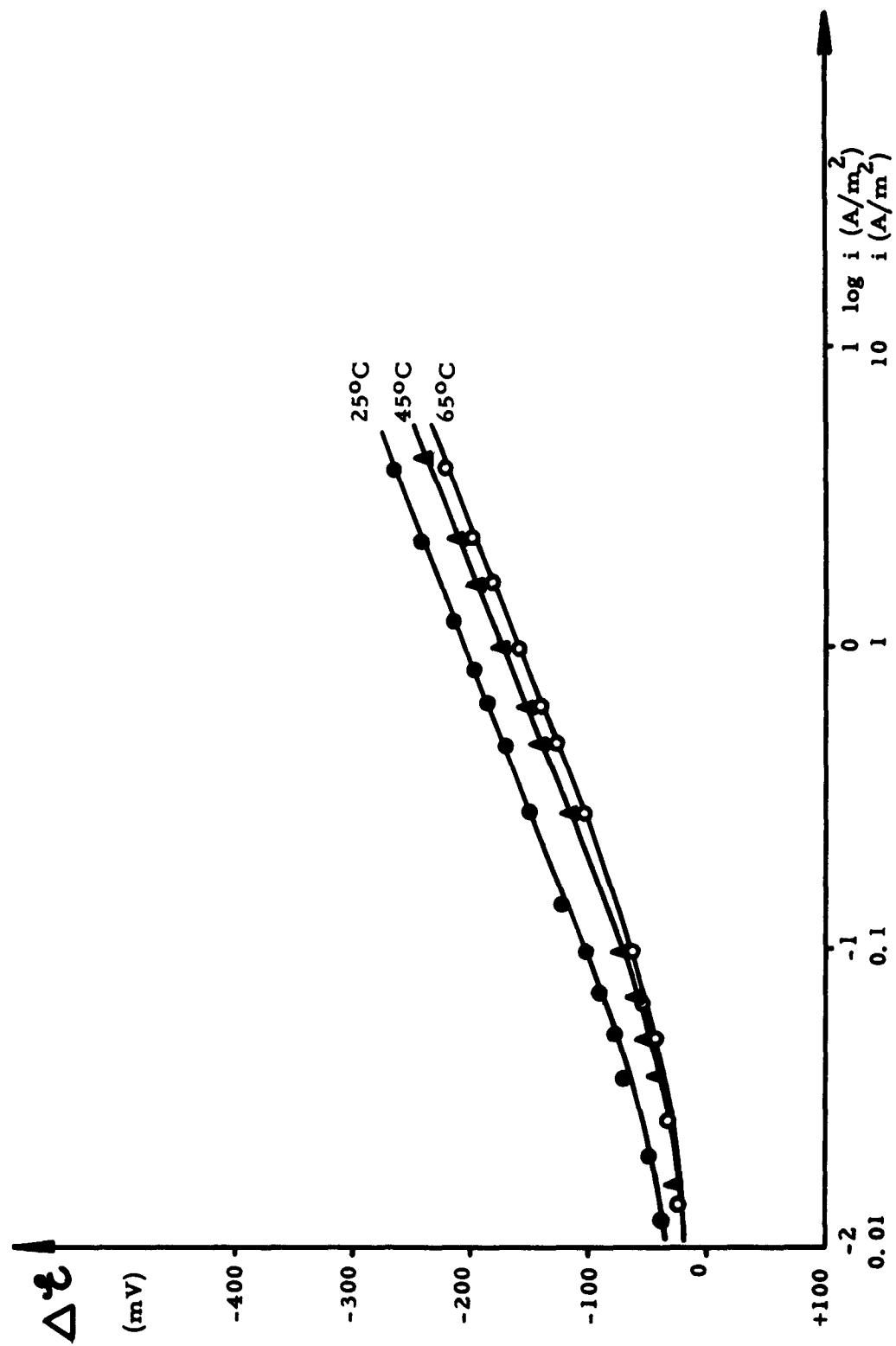
Fig. 13 - (100) Ni/0.003 M HCl

Fig. 14 – (110) Ni; t = 45°C

0.005 M HCl
0.150 M HClO$_4$
0.100 M H$_2$N-SO$_3$H
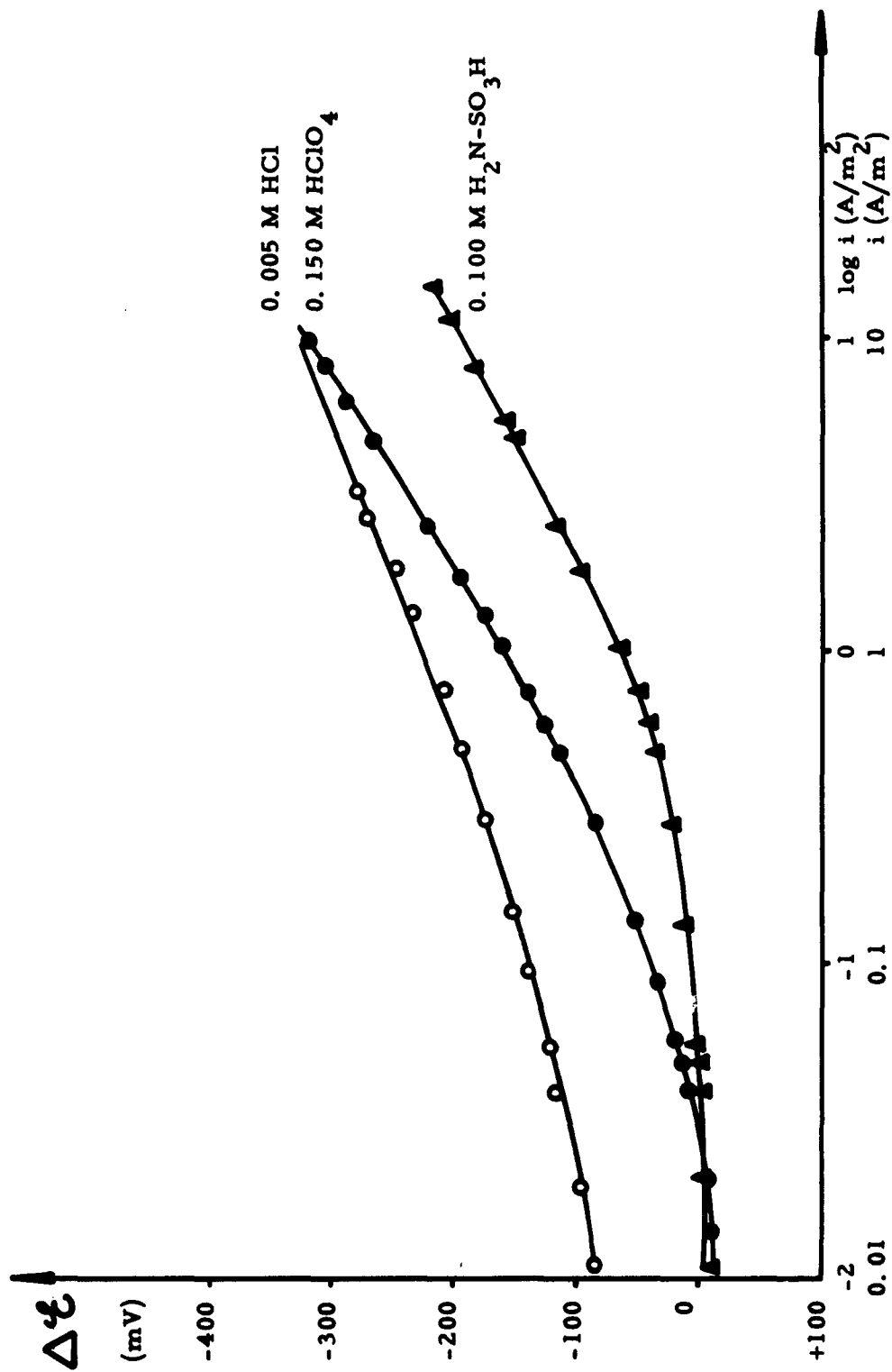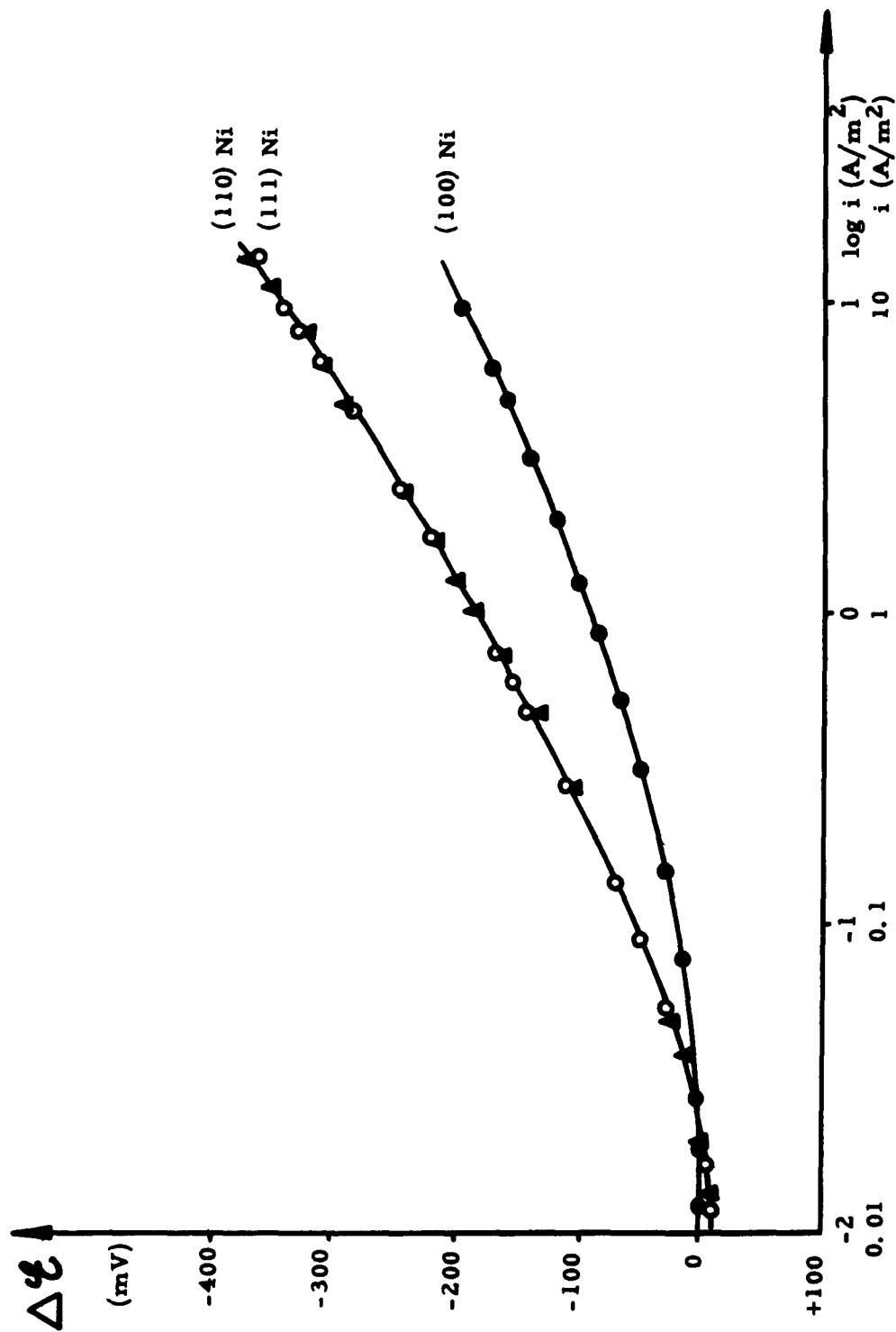
Fig. 15 – Behavior in perchloric acid; t = 25°C
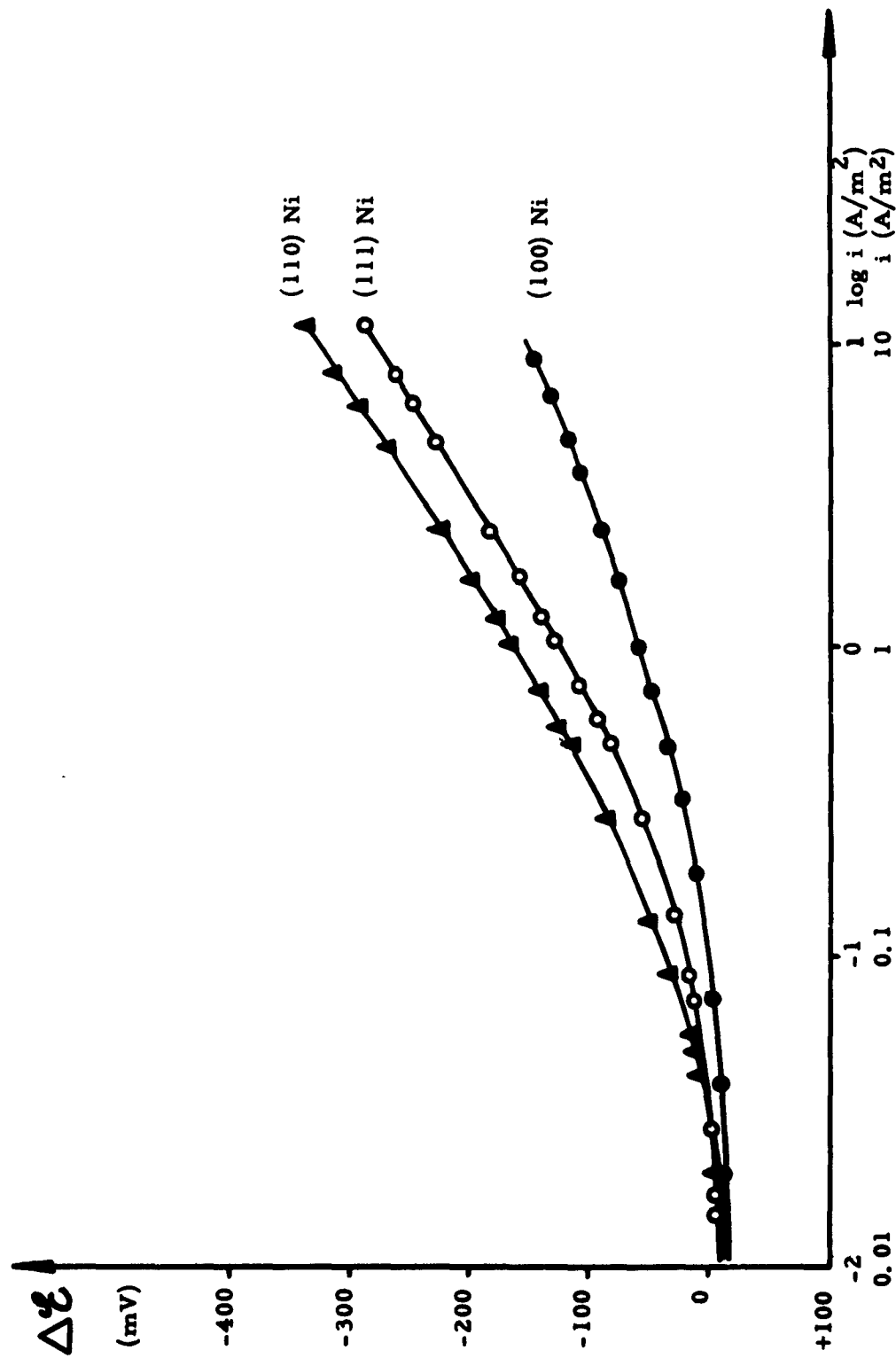
Fig. 16 – Behavior in perchloric acid; t = 45°C
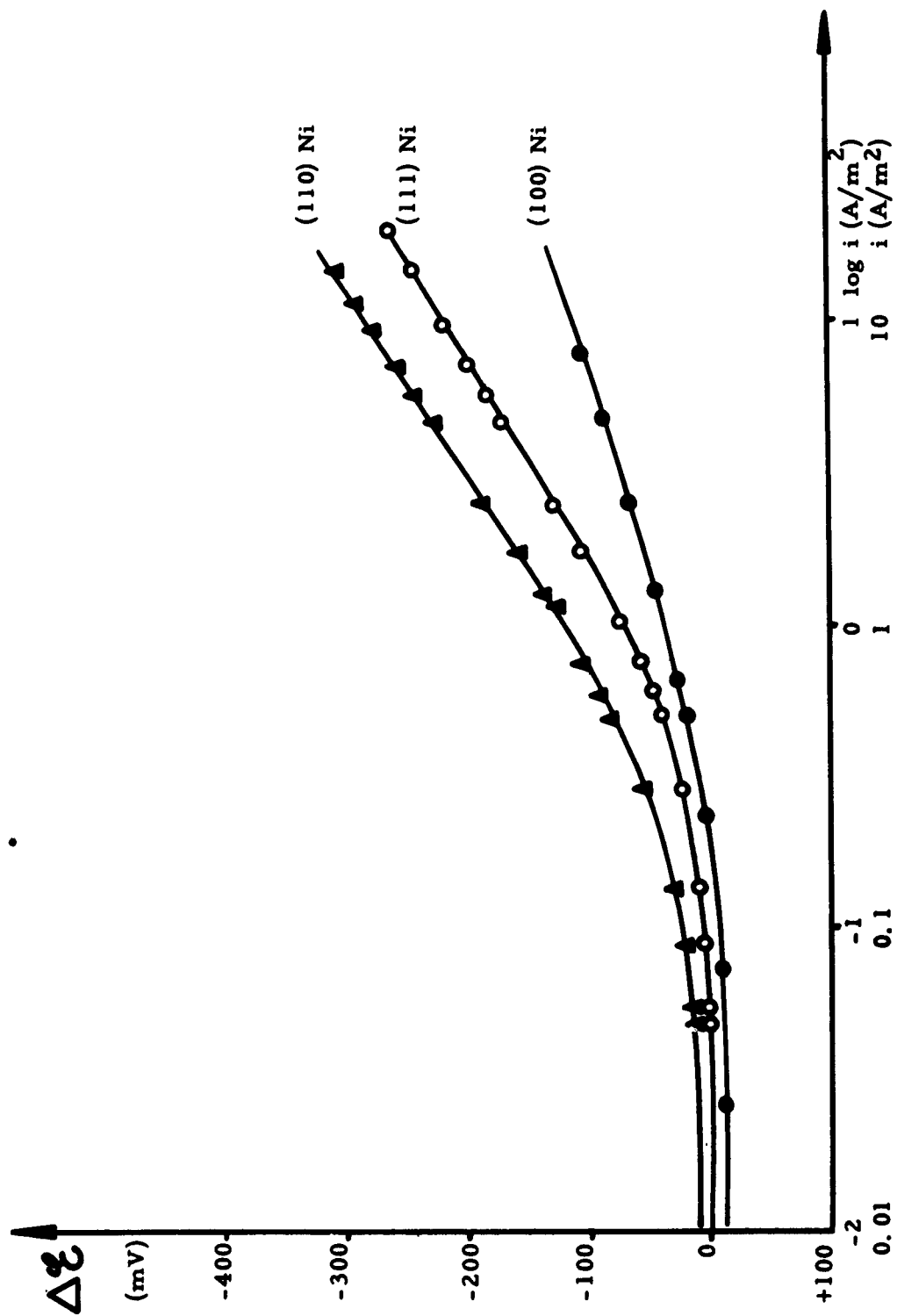
Fig. 17 - Behavior in perchloric acid; t = 65°C
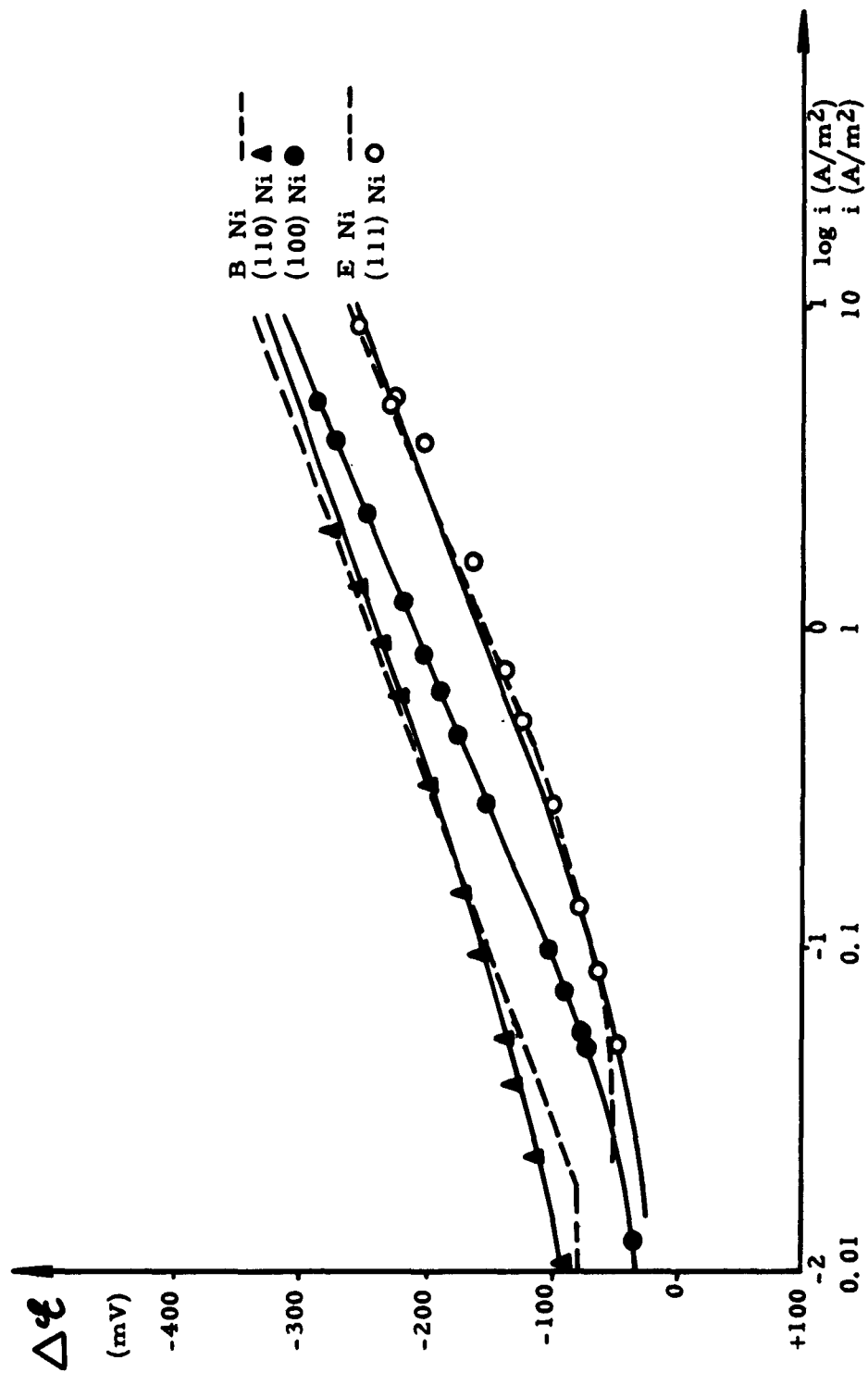
Fig. 18 - Behavior in hydrochloric acid; t = 25°C
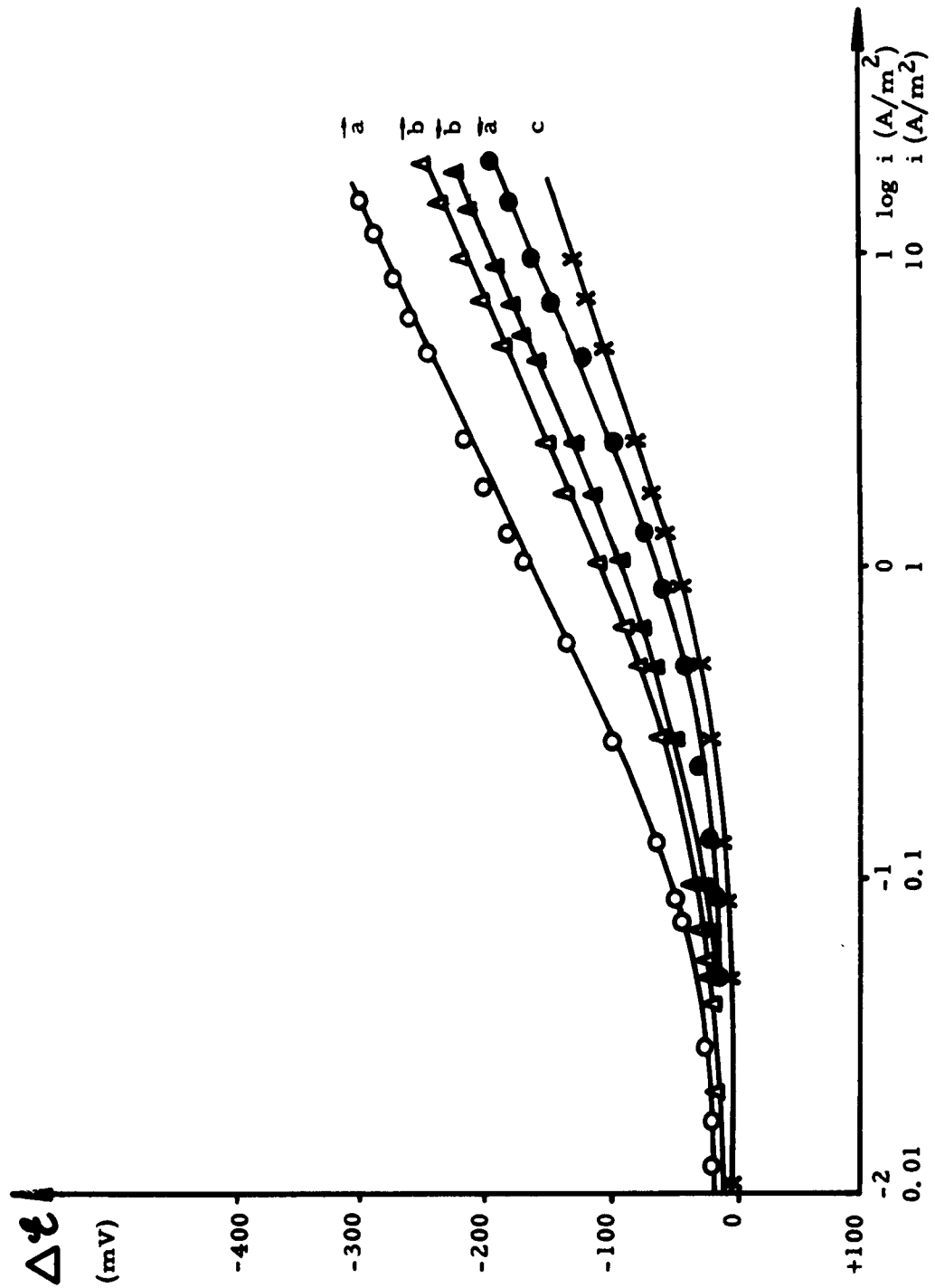
Fig. 19 - (111) Ni/0.1 M H$_2$N-SO$_3$H; t = 25°C
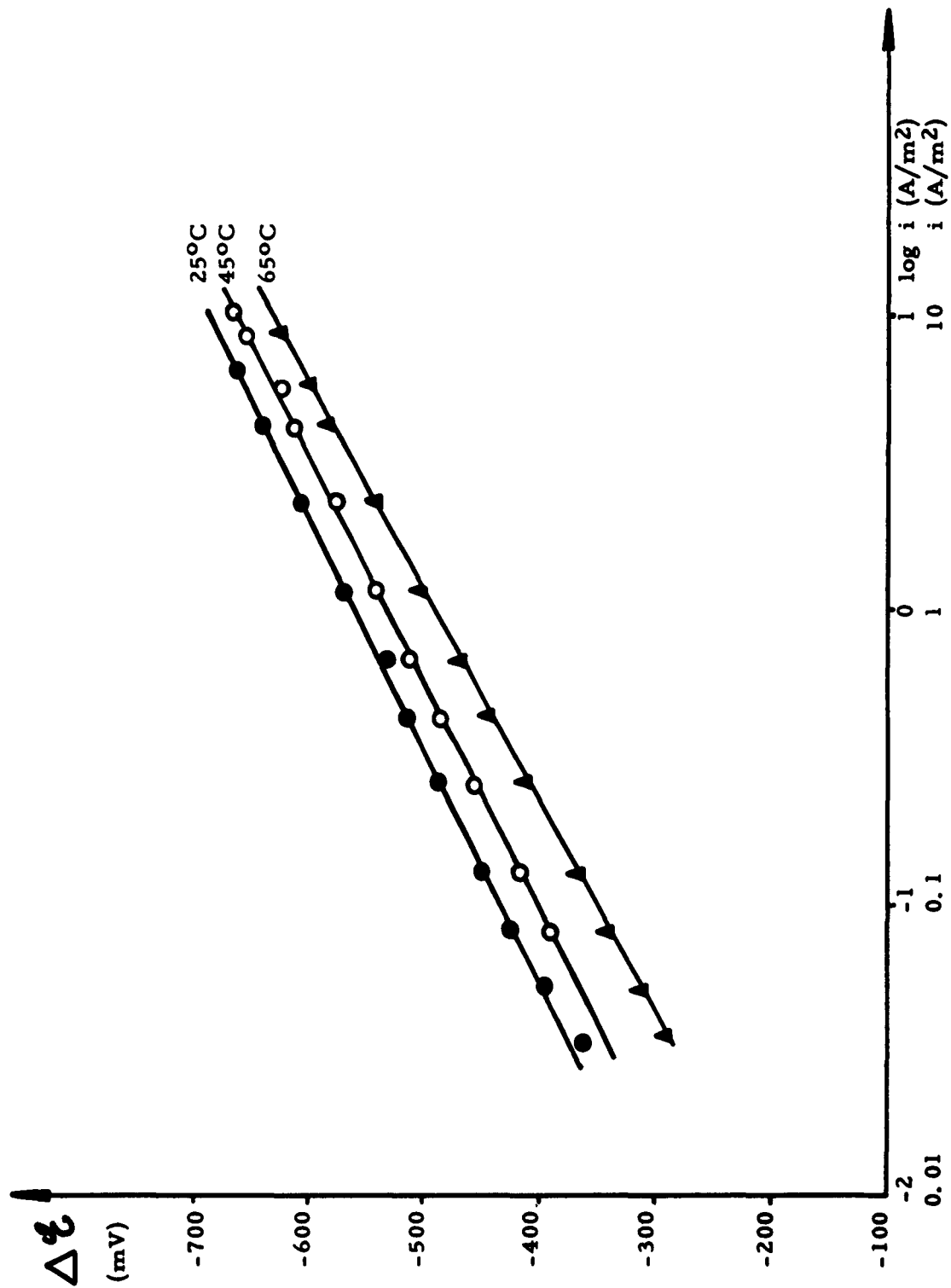
Fig. 20 – Polycrystalline Sn/HClO$_4$ 0.03 M
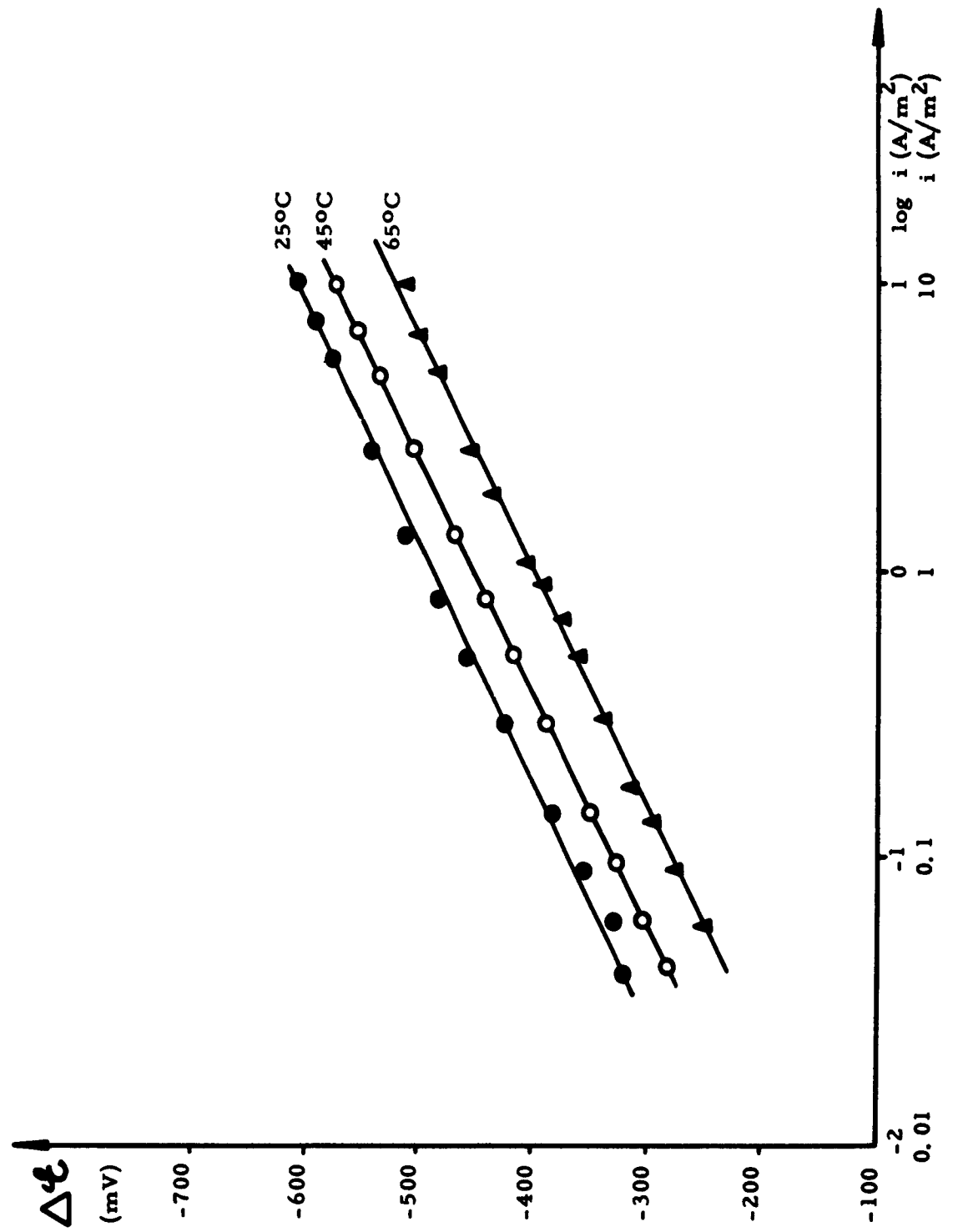
Fig. 21 - (001) Sn/HClO$_4$ 0.08 M
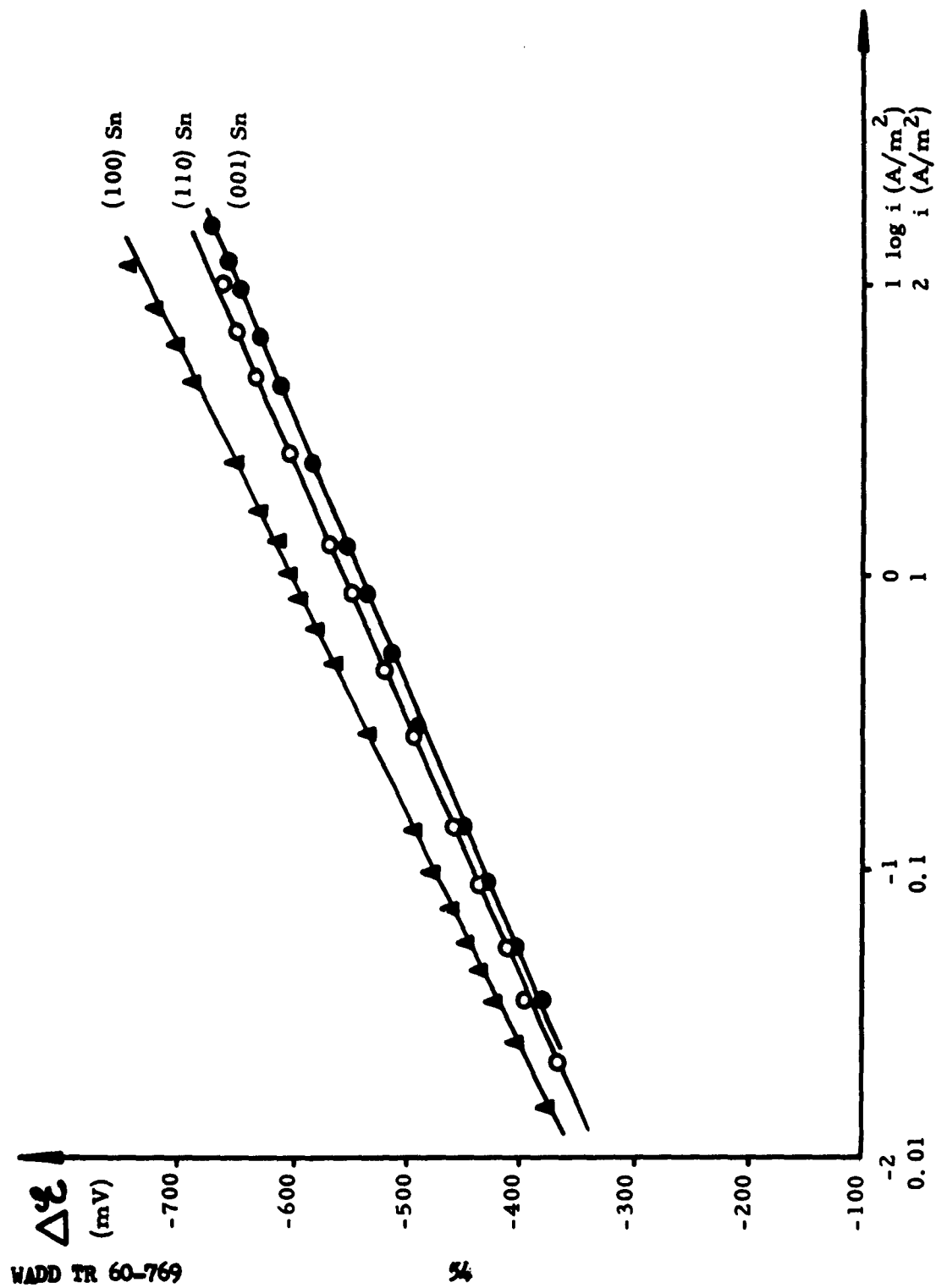
Fig. 22 – Behavior in 0.01 M perchloric acid; t = 30°C
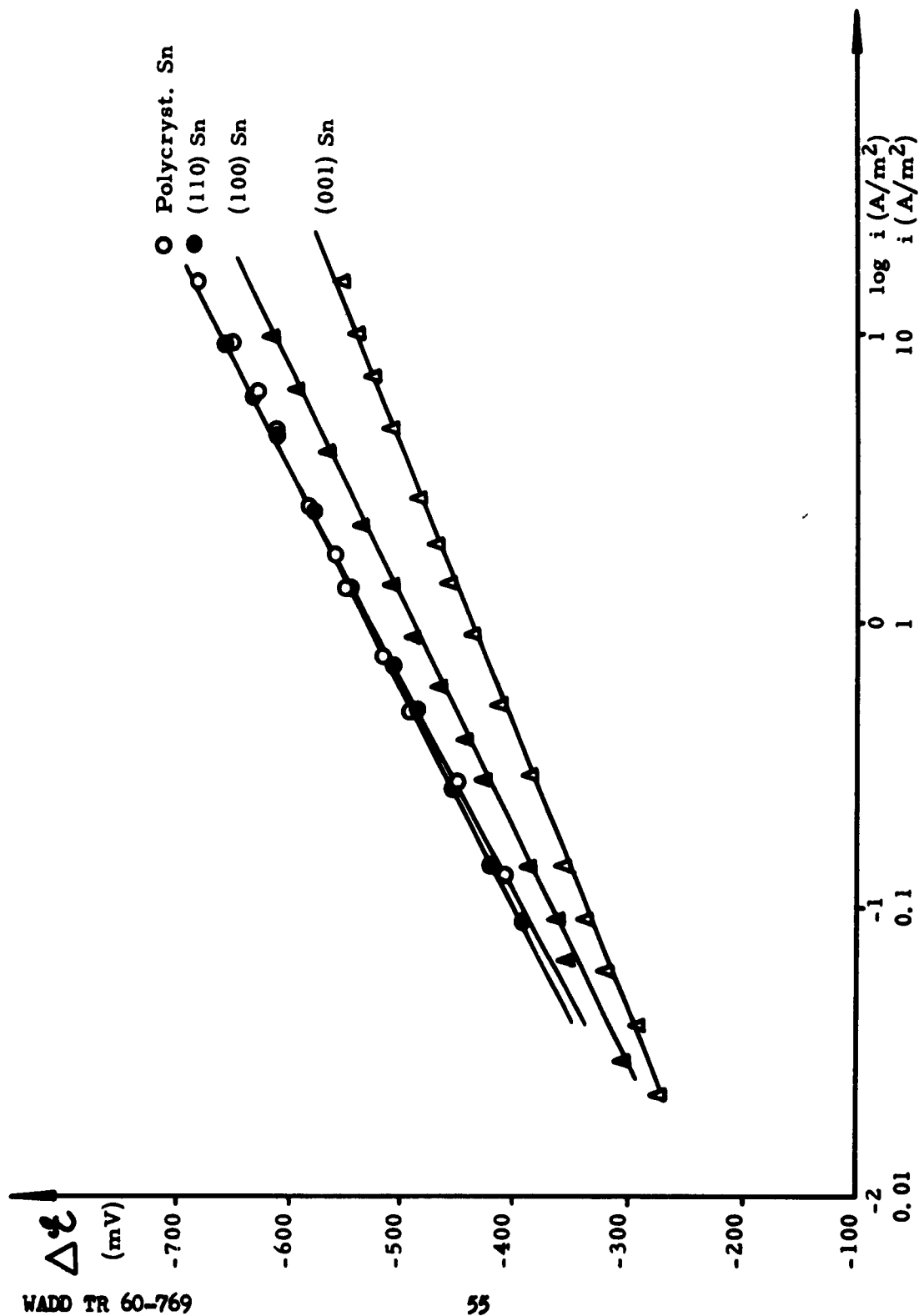
Fig. 23 – Behavior in 0, 03 M hydrochloric acid; t = 65°C

Fig. 24 - (110) Sn; t = 65°C

0.01 M HClO$_4$

0.08 M HClO$_4$

$\Delta\xi$ (mV)

log i (A/m^2)

i (A/m^2)

Fig. 25 - (110) Sn; t = 45°C
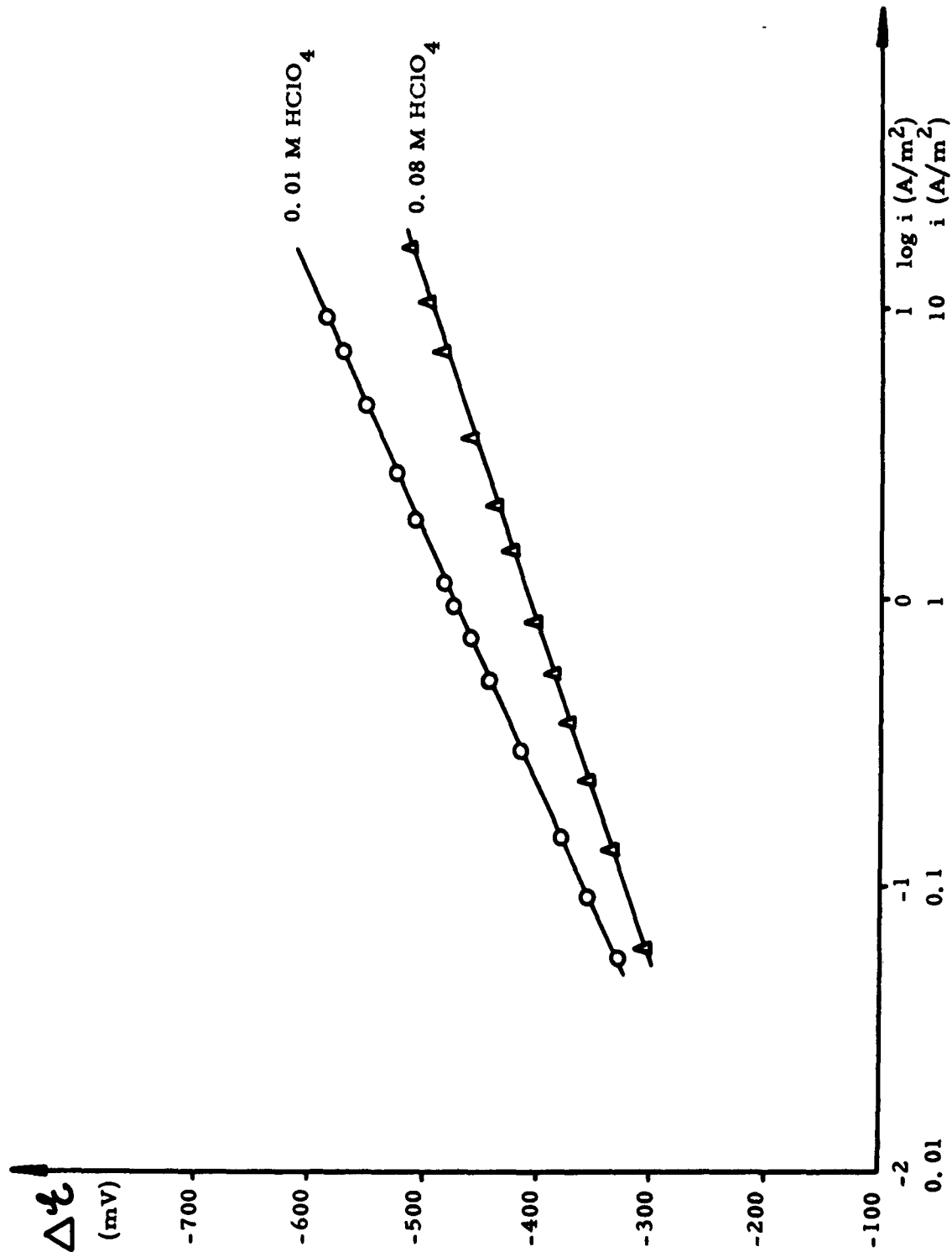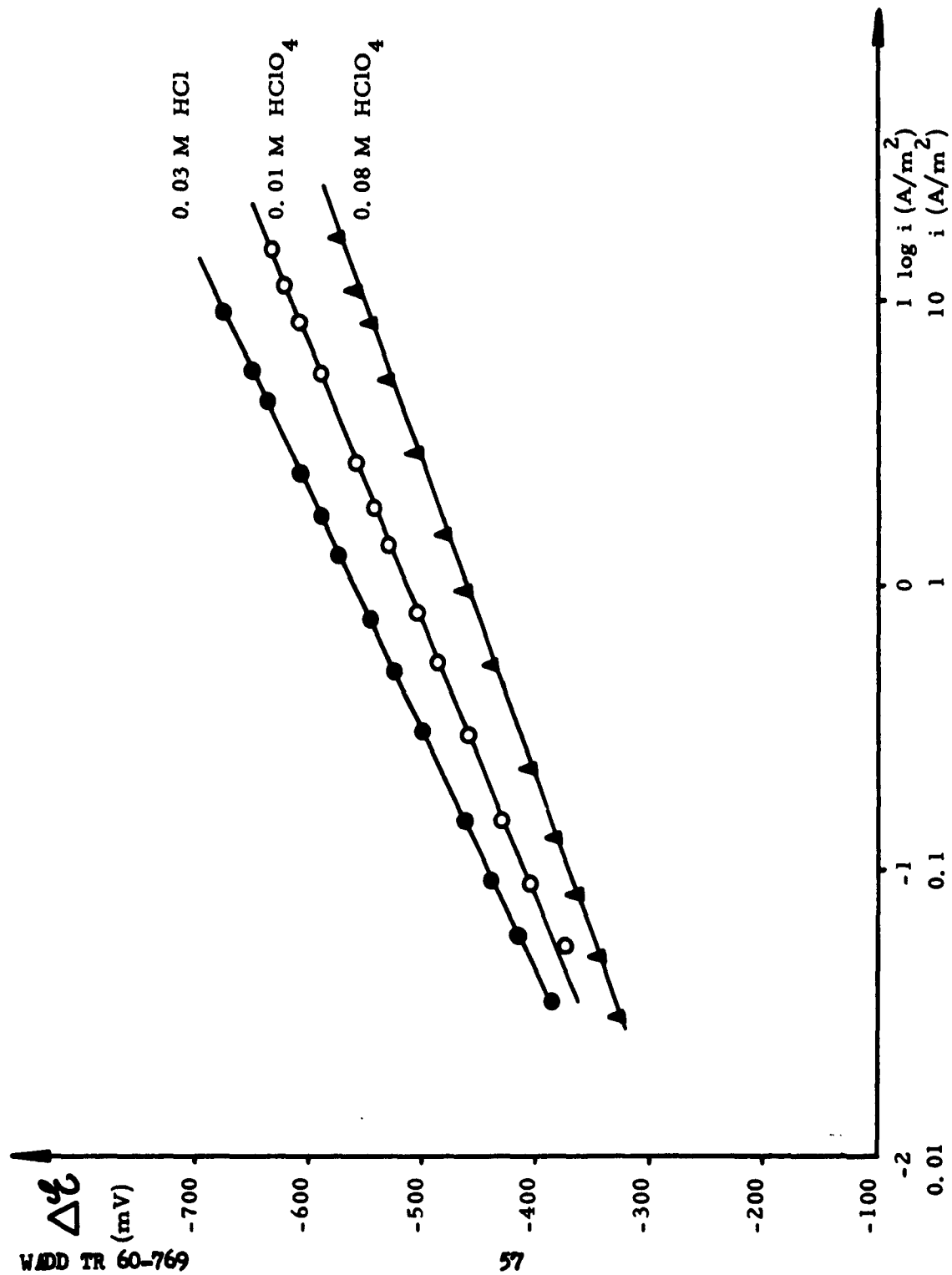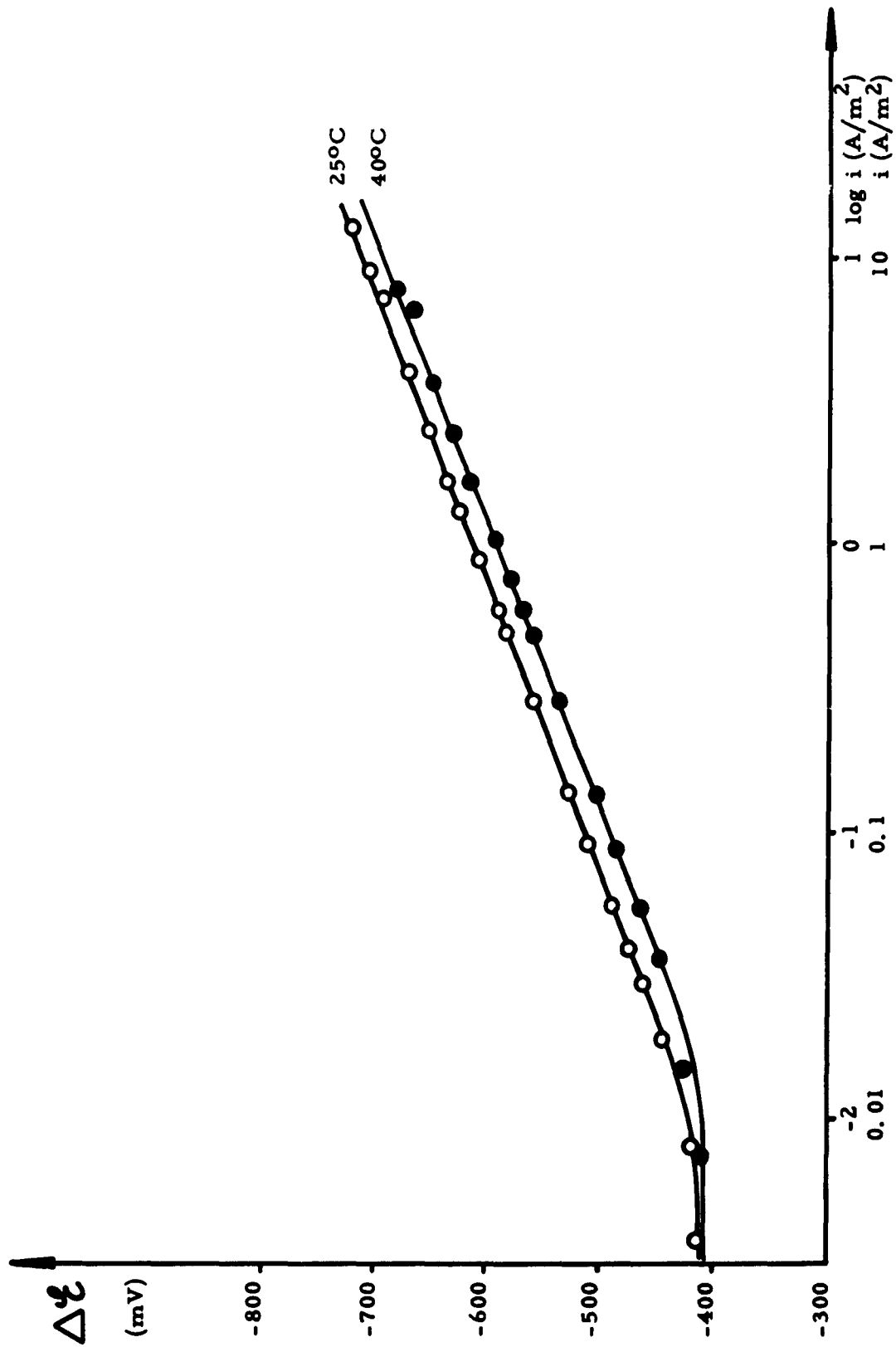
Fig. 26 - (10I0) Cd/ 0.020 M HClO$_4$
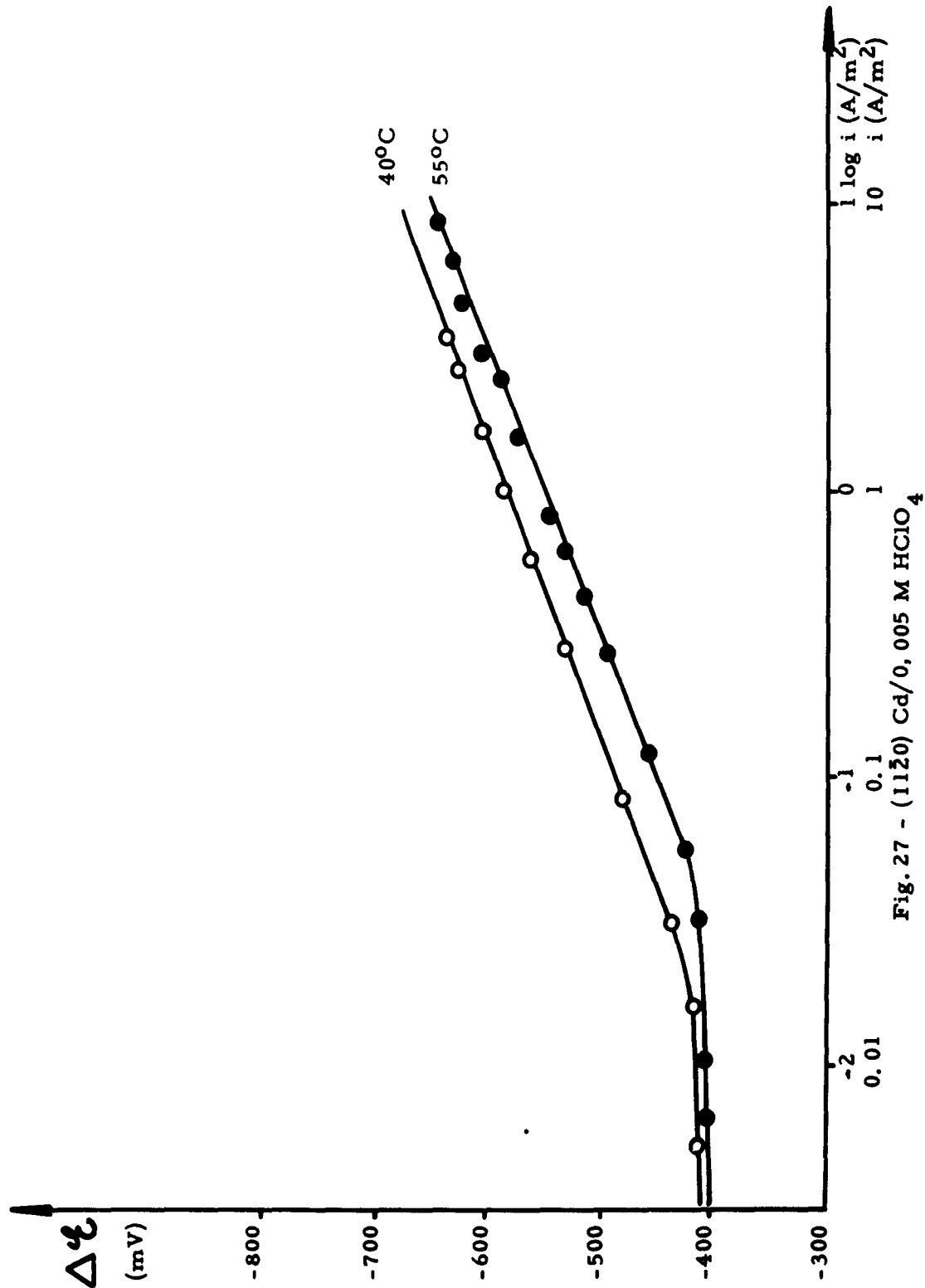
Fig. 27 - (11Z̄0) Cd/0, 005 M HClO₄
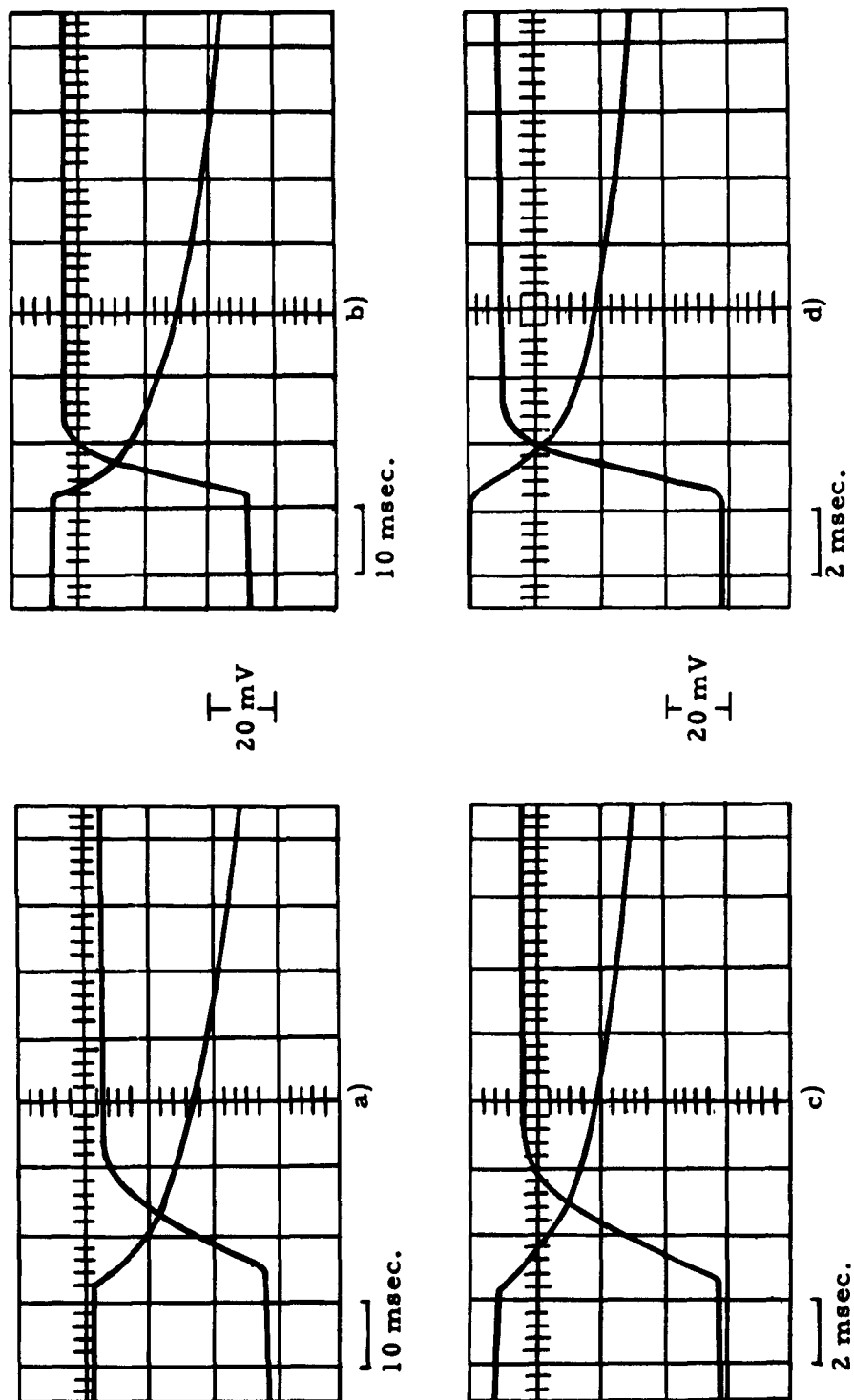
Fig. 28 - Overvoltage versus time oscillograms (0001) Cd/0, 035 M HClO$_4$
a) i = 3 A/m^2; b) i = 5 A/m^2; c) i = 10 A/m^2; d) i = 30 A/m^2
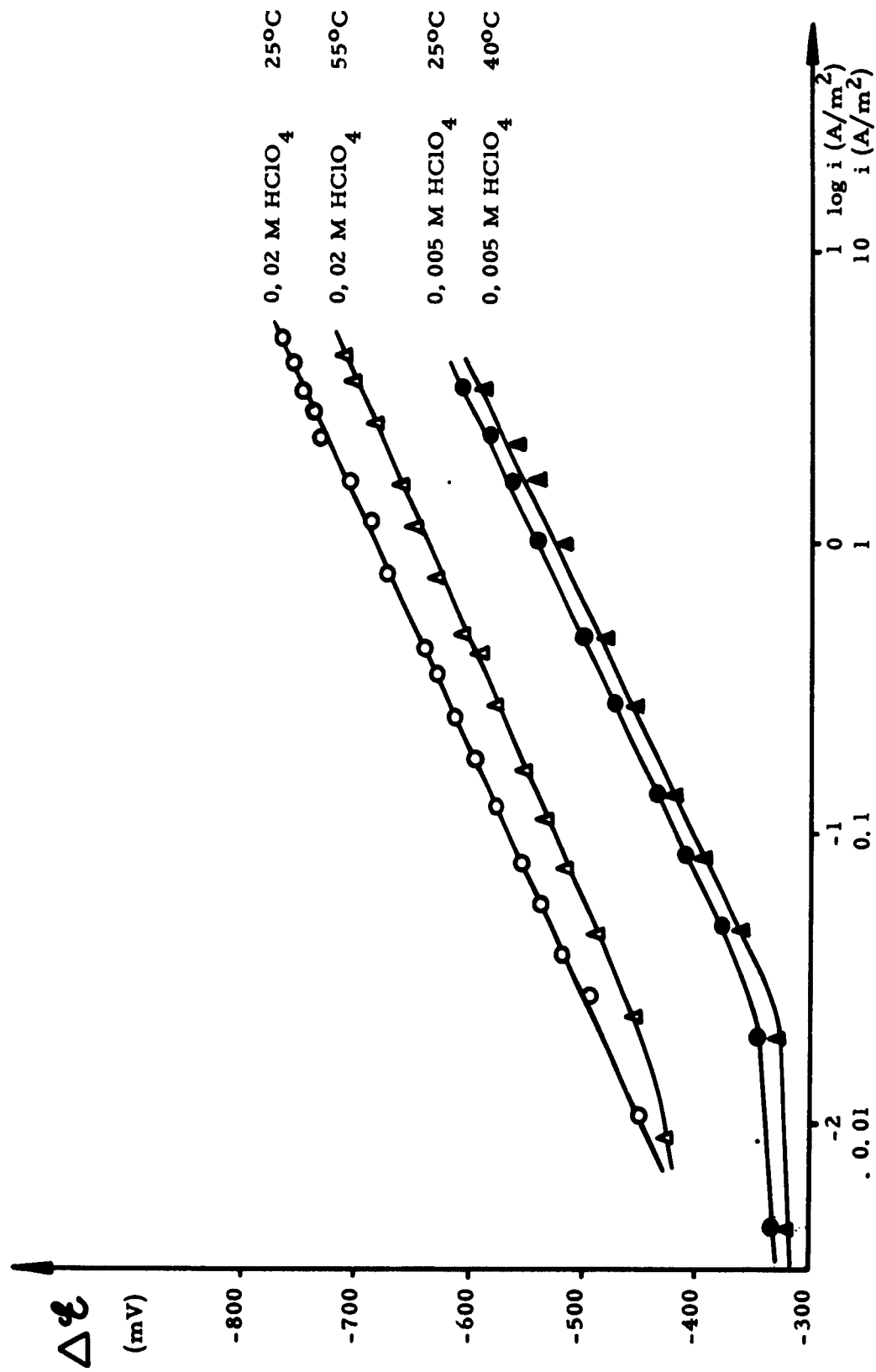
Fig. 29 - (0001) Cd/HClO₄
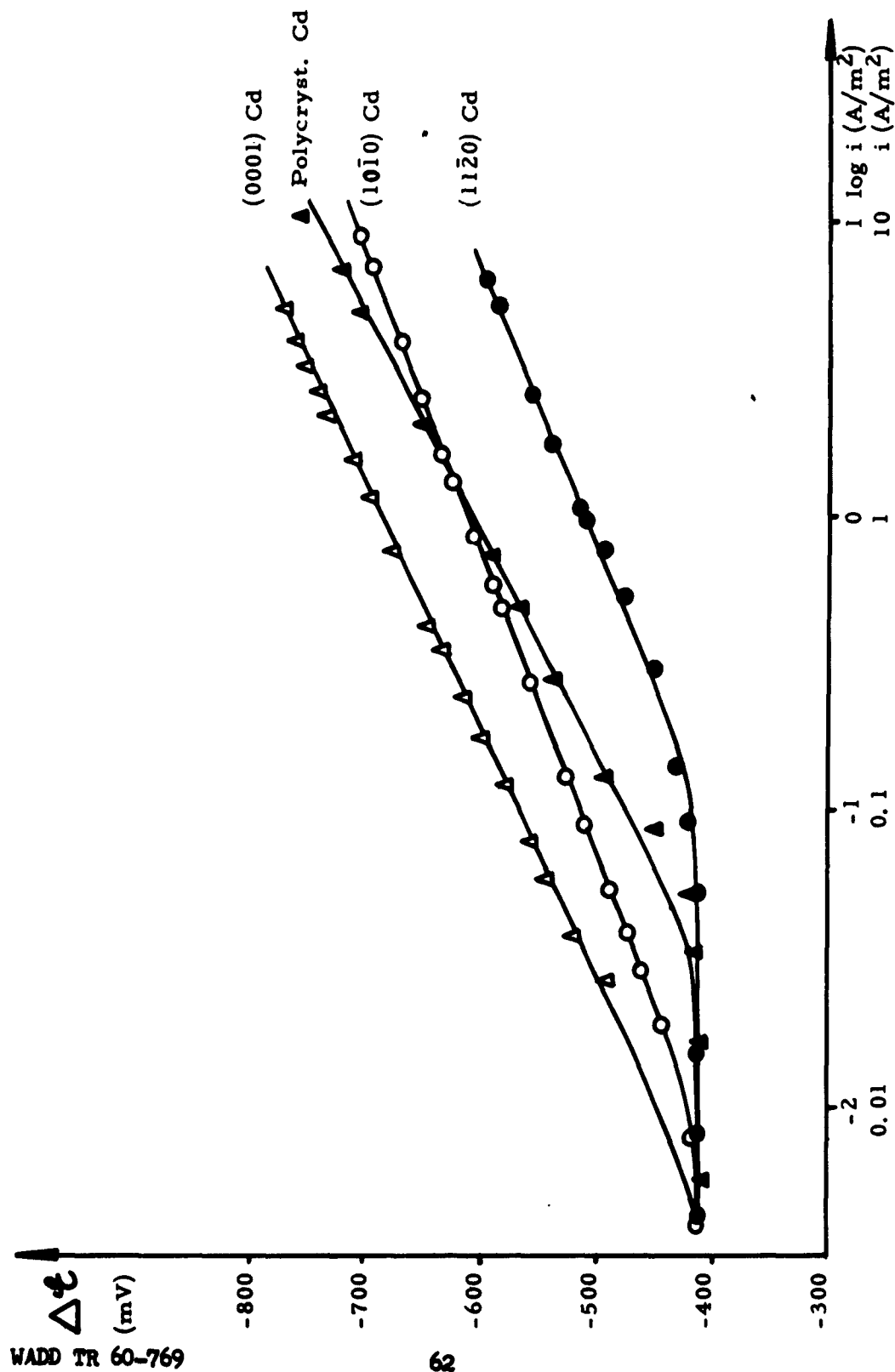
Fig. 30 - Behavior in concentrate perchloric acid.   t = 25ºC

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e Metallurgia del Politecnico di Milano -
Milano, Italy, USAF, Air Research and Develop-
ment Command, European Office, Brussels,
Belgium - RESEARCHES ON HYDROGEN OVERVOLTAGE
ON METALLIC SINGLE CRYSTALS, by R. Piontelli,
L. Peraldo Bicelli, and A. La Vecchia.
February 1961, 62 pp incl. fig. & tables.
(WADD TR 60-769) (Project No. 7022; Task No.
73660)(Contract No. AF 61(052)-144)
Unclassified report

Hydrogen overvoltage on silver, lead, nickel,
tin and cadmium single crystals has been
measured in different experimental conditions.
The results have been discussed and it has
been observed that the Tafel law is general-

(over)

ly followed.